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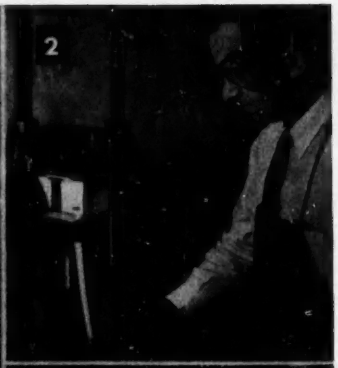

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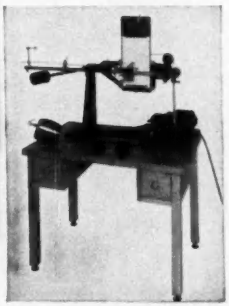

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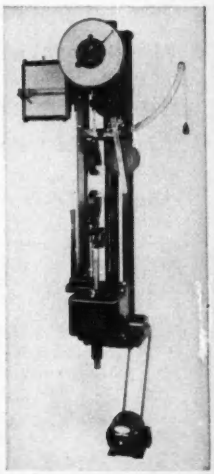

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TEXTILE RESEARCH JOURNAL

VOL. XXI, No. 1 January, 1951

Mechanical Hysteresis Properties of Single Fibers and Cords

Helmut Wakeham* and Edith Honold†

Institute of Textile Technology, Charlottesville, Virginia

Abstract

An apparatus for stretching and relaxing single fibers for the purpose of determining mechanical hysteresis losses is described. Results obtained on cotton, viscose rayon, and nylon fibers are compared with similar data previously obtained on cords from which the fibers were taken. Such comparison indicates that interfiber friction is probably the major cause of hysteresis energy losses in cotton and rayon tire cords under cyclic loads at low frequencies.

THE LIFE of most textile products is best described as a succession of cyclic processes, a series of strains interspersed with periods of relaxation, with some degree of recovery between successive strains. Consequently, the physical properties evaluated during cyclic deformation are probably more important life determinants than are those properties derived from single or static tests. Among the properties which may be evaluated from cyclic-deformation studies are mechanical hysteresis, or energy loss, and elastic modulus, or the stress necessary to produce a definite strain. A comparison of these under conditions of cyclic loading for different textile fibers may contribute to a better understanding of the constitution of these fibers and their adaptability to different uses.

Hysteresis and related elastic properties have been extensively studied for native and mercerized cotton, rayon, and nylon in the form of tire cords [1, 3, 5, 6, 7, 9]. The methods used involved the study of resonant vibrations at sonic frequencies as well as the actual determination of simultaneous load and elongation values. But, with the exception of an investigation of rayon tire cords by Breazeale and Whisnant [1], interpretation of the

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results was complicated by the unknown contribution of cord construction to the answers obtained. Hence, a similar study of the hysteretic properties of the individual fibers and filaments within the cord was indicated.

The present study was undertaken, therefore, not only to obtain basic data on the hysteresis behavior of different textile fibers, but also to obtain some further insight into the effect of cord and yarn construction on physical behavior during cyclic deformation.

Experimental Procedure

The fibers and filaments used in this study were obtained from the cotton, rayon, and nylon tire cords that were used in the previous investigation [3].

The apparatus, which essentially is a miniature of that used on tire cords, is shown in Figure 1. In brief, the fiber was mounted in series with a calibrated Pyrex glass spring,* and tension cycles at the rate of 1 per sec. were applied to the fiber through the spring by means of a motor-driven, adjustable eccentric. The positions of the upper end of the fiber—the lower end was fixed (see Figure 1)—and the upper end of the spring, as indicated by a small pointer extending through the spring to the top of the fiber, were recorded throughout the cycle by means of a motion picture camera on 16-mm. film. These positions were read from the film with a low-power microscope equipped with a filar micrometer eyepiece. A curve of position *vs.* frame number was plotted for each cycle to be computed, and the instantaneous load and elongation were calculated from the position data at suitable intervals around the hysteresis loop.

The load-elongation loops were integrated graphically with a planimeter to obtain areas which could be simply converted into hysteresis energy losses in ergs or any desired unit. The authors have followed the practice of expressing hysteresis in energy loss per unit weight of textile material in order to facilitate comparisons between fibers and yarns. The elastic modulus was calculated from the over-all slope of the hysteresis loop, as described earlier [9].

Determination of the initial fiber length for the elongation calculation was made in each case by means of a cathetometer, with a known tension on the fiber. The cotton fiber cross-sectional area, for elastic modulus computations, was evaluated from the averages of the areas of the photomicrographs of the fiber sectioned at various places throughout its length. For the nylon and rayon filaments, cross-sectional areas were calculated from measured grex values.

The Pyrex spring was calibrated with a cathetometer, using small lengths of wire the weights of which were determined by means of an analytical balance.

It was found that by using the method described above the fiber extension could be determined with an accuracy of 0.001 mm.; the fiber tension within 0.5 mg. Of these two sources of error, the uncertainty in the hysteresis resulting from the extension error was by far the more serious. The maximum error in the hysteresis was about 0.4×10^4 ergs/g./cycle, and in elastic modulus it was about 1×10^{10} dynes/cm.^{2}. The probable errors are undoubtedly somewhat less than the above, because in drawing the smoothed hysteresis

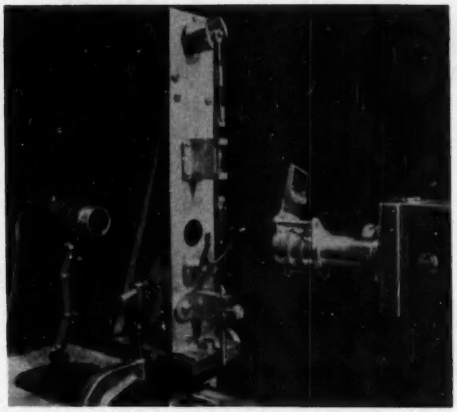

FIG. 1. *Single-fiber hysteresis apparatus. In the center, from top to bottom, are the adjustable eccentric, which is driven by a small synchronous motor; the drive shaft, of adjustable length; the shaft guide; the Pyrex spring, with the spring pointer projecting down the middle into the field of view of the camera; the fiber under test; and the lower adjustable hook for holding the lower end of the fiber in a fixed position. The lamp used for silhouetting the top of the fiber and the spring pointer is to the left; the motion picture camera is to the right of the apparatus.*

* Quartz is to be preferred for this application, but the Pyrex glass springs were more easily constructed and were sufficiently elastic for the present purpose.

loop plus errors are compensated in part by minus errors.

The fibers were tested at a frequency of 1 cycle per sec., with the load range from about 0.1 to 0.4 g./grex, in order to permit a comparison with the results for the cords previously tested. All tests were made at room conditions, approximately 25°C and 45% relative humidity. Hysteresis loops were calculated for the 10th and 10,000th cycles. In the experiments with cords reported previously [9], it was found that hysteresis varied approximately linearly with the logarithm of the number of cycles. Thus, the average of the values calculated for the fibers could be compared directly with the 1,000th-cycle results obtained for the cords.

Results

Typical results on cotton, viscose rayon, and nylon fibers are given in Table I. Because it was not possible to determine the grex number of the cotton fibers until after testing, some difficulty was encountered in selecting load ranges for these fibers to meet the 0.1 to 0.4 g./grex load-range specification.

In Table II is a comparison of elastic data for these fibers and for the corresponding cords from which they were taken. In this table hysteresis values are reported in cals. per g. of fiber or cord instead of in ergs per g.

Discussion and Conclusions

The hysteresis data for cotton in Table I illustrate the wide variations between individual fibers, which are to be expected in view of the large differences in cross-sectional areas and shapes of single cotton fibers. These individual differences compound the difficulties encountered by the investigator who is trying to establish characteristic physical properties of the fiber. In the present case it is impossible to tell whether the wide variation in hysteresis values is due to the small differences in load ranges applied or to differences in structural shape factors between fibers. Furthermore, the grex numbers of the fibers may be in error by as much as 10%. But in spite of these difficulties, it seems reasonable to assign mechanical hysteresis values of the order of 1.3×10^4 ergs/g./cycle to the larger, more mature cotton fibers at the cyclic-load conditions indicated.

TABLE I. HYSTERESIS DATA ON COTTON, RAYON, AND NYLON FIBERS

Fiber type	Grex No.	Load cycle (g.)	Load cycle (g./grex*)	Hysteresis (ergs/g./cycle)	Elastic modulus (dynes/cm.²)
Cotton	1.6	0.12–0.63	0.08–0.40	4.6×10^4	13.3×10^{10}
	2.0	0.12–0.64	0.06–0.32	2.5	11.3
	3.0	0.36–0.83	0.12–0.28	1.2	7.9
	3.4	0.15–0.67	0.04–0.20	1.3	10.0
	4.0	0.27–0.75	0.07–0.19	1.3	7.3
Viscose rayon	2.5	0.15–0.95	0.06–0.38	3.1	16.3
	2.9	0.11–0.90	0.04–0.31	3.6	14.5
Nylon	5.8	0.69–2.81	0.12–0.48	17.2	5.76

* The grex unit is defined as the weight in grams of 10,000 meters of fiber, yarn, or cord. See A. G. Scroggie, TEXTILE RESEARCH JOURNAL 19, 292–6 (1949).

TABLE II. COMPARISON OF ELASTIC DATA FOR FIBERS AND CORRESPONDING TIRE CORDS*
(25° C AND APPROXIMATELY 45% R.H.)

Tire cord identification	Fiber type	Hysteresis (cal./g./cycle) Fiber	Hysteresis (cal./g./cycle) Cord	Elastic modulus (dynes/cm.²) Fiber	Elastic modulus (dynes/cm.²) Cord
C-3	Cotton	0.5×10^{-3}	5.3×10^{-3}	$10. \times 10^{10}$	5.4×10^{10}
R-3	Viscose rayon	0.73	5.74	16.3	4.24
N-1	Nylon	4.11	6.48	5.76	4.85

* Tire-cord hysteresis data reported [3] are for the same materials at similar test conditions of 0.1–0.4 g./grex load cycles and of ambient temperature and relative humidity reported herein.

Under similar conditions the rayon filaments exhibit a somewhat higher energy loss. The lower values for cotton may be explained by the relatively high degree of crystallinity assigned to cotton as compared to that for rayon [2, 4], for it is recognized that crystals are more perfectly elastic than are amorphous substances. In the textile fiber the "internal friction" which gives rise to mechanical hysteresis is probably due to movement of the fiber molecules with respect to each other. Because the molecules are strongly attracted to each other in crystalline regions, such motion is mainly limited to the intercrystalline parts. Hence, most of the hysteresis energy loss probably occurs in the amorphous fraction of the fiber.

Rayon and cotton tire cords appear to have mechanical hysteresis losses about 8 and 10 times greater than those of their constituent fibers, respectively. (See Table II.) This suggests that most of the energy loss in stretching and relaxing of the cord is due to *interfiber* friction between moving cord components, and that only a small part is due to the imperfect elasticity of the fibers themselves. In the case of nylon cord, with its relatively low twist count and slick nylon fibers, the hysteresis of the fibers is almost as high as that of the cords. Most of the energy loss in the nylon cord is probably due to internal friction within the fibers.

It is interesting to note that Lyons [5] made a similar comparison of the hysteretic properties of single viscose rayon and nylon yarns and of the corresponding tire cords at a cyclic frequency of 180 c.p.s. For rayon, the energy losses per unit stress amplitude of the yarn and cord were in the ratio of 0.45 to 0.62, whereas for nylon the ratio for yarn to cord losses was 1.15 to 1.08. Thus, even at much higher frequencies the inter-component friction in the cord construction is appreciable for rayon but negligible for nylon.

The wide variations in hysteresis values for cotton fibers are accompanied by equally great differences in their elastic moduli (see Table I). Here again, these differences are believed to be larger than those caused by inevitable errors in determining the grex number and in the measurement of the hysteresis loop. Hence, they must be ascribed to individual differences between the fibers.

The data of Table I show further that, in general, for comparable load cycles the viscose rayon has a higher elastic modulus than cotton has. This result on single fibers confirms the observations of Palandri [7] and of Lyons and Prettyman [6], who reported values at higher frequencies of cyclic loading. The reverse might be expected on the basis of the higher crystallinity of cotton, for it is generally believed that the extension in high polymers exhibiting low elastic moduli occurs in the noncrystalline regions. Rose and Griffiths [8] and Work [10] have shown, however, that elastic modulus, as determined from a static test, is also directly related to crystallite orientation in the fiber. This effect very probably exists in cyclic extension as well, and serves to suggest that the higher elastic modulus of the tire-cord rayon over cotton is due to the high degree of crystallite orientation imparted to the rayon fiber during manufacture.

In all cases compared herein, the elastic modulus for the tire cord is lower than that for the corresponding constituent fiber (Table II). The loose structure of the cord or yarn tightens up upon stretching, thereby giving rise to greater extension than would be exhibited by the fiber alone for a comparable stress. This result is also noticeable at 180 c.p.s. according to the data of Lyons [5]. The dynamic stretch moduli for yarn and cord, respectively, are reported as: rayon, 19.7 and 15.2; nylon, 9.8 and 8.7 ($\times 10^{10}$ dynes/cm.^{2}).

As a result of the present investigation it might be concluded that, in general, for the low frequencies of cyclic loading herein reported, the hysteresis and elastic properties of the cords and yarns tested are largely characteristic of their constructional features. Apparently, at high frequencies of cyclic loading the motion between component parts of the cord cannot readily take place, and the elastic modulus and hysteresis observed are characteristic of the material of which the cord is composed. For example, the elastic moduli for cotton, viscose rayon, and nylon tire cords at 180 c.p.s. are very nearly the same as the moduli for the fibers at 1 c.p.s. At low frequencies the interply and interfiber motion in the cord is appreciable, resulting in a lower elastic modulus and a higher hysteresis energy loss for the cord than for the fiber.

Summary

An apparatus for measuring simultaneous load and elongation values for single textile fibers throughout elongation cycles imposed at the rate

of 1 per sec. has been described. With this apparatus, data have been obtained which permit plotting the mechanical hysteresis loops for single cotton, rayon, and nylon fibers or filaments, and calculating their hysteresis energy losses and elastic moduli under the conditions of test. These properties for the single fibers were compared with the same properties for the cords from which the fibers were obtained, using comparable test conditions. Such comparison indicates that (1) in general, cotton fibers have lower hysteresis energy losses and lower elastic moduli than do corresponding tire-cord rayon fibers; (2) the hysteresis energy losses for cellulose fibers and filaments (in cals. per g.) are 8 to 10 times lower than the corresponding losses for tire cords of the same materials; and (3) the elastic moduli for the cellulose fibers are 2 to 4 times larger than the moduli values of the cords. These results suggest that for cotton and rayon, most of the cord hysteresis is due to interfiber friction between moving cord components. In the nylon cord of low twist, the properties of the cord are very nearly the properties of the constituent filaments.

Acknowledgment

The authors are pleased to acknowledge the assistance of Miss Anne Brown in the measurement and calculation of the data reported, and of Dr. Earl K. Fischer for the photograph in Figure 1.

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(*Manuscript received June 19, 1950*)

The Relation of Length to Other Physical Properties of Cotton Fibers

Ora W. Morlier, Rollin S. Orr, and James N. Grant

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Abstract

Results are reported on tests of breaking load and elongation of single fibers at constant specimen length from the length groups of 6 cotton samples. A description is given of the instrument used in these tests. Average weight fineness of the center section of fibers from each length group was determined, and the tenacity and "stiffness" of the fibers were calculated.

A method is described of calculating a single-fiber tenacity "index" for a cotton sample from the tenacity values of 3 modal-length groups. A high correlation is demonstrated between this index and the weighted mean single-fiber tenacity for the whole sample.

IN A PREVIOUS PUBLICATION [3] data were presented on the strength of single cotton fibers from 4 varieties of American Upland cotton. It was demonstrated that fiber breaking load and tenacity (specific strength) increase with increase in length of the individual fibers, and that an inverse relationship exists between fiber tenacity and the length of the section tested. These data were used to interpret some of the variations in flat-bundle test results.

While many data have been published on the physical properties of single fibers [2, 4, 6–10], little information is available on the variation of these properties with fiber length within a single sample for American Upland cottons. In most strength tests made on cotton, whether of the bundle or of the individual-fiber type, the preparation of the sample alters the length distribution, so that the sample broken is not necessarily representative of the actual length distribution of the cotton. The results would therefore not be expected to be truly representative of the strength of the cotton. While this is true of either type of test, results obtained using the bundle-type test are more liable to error than are those from the single-fiber type in the comparison, for example, of chemically modified and raw samples, since the results of the bundle test are dependent to some extent upon the surface characteristics of the sample.

In the present paper the results of a more extended investigation on the relation of tenacity of single fibers to fiber length are reported, and the instrument used in making the tests is described. The tenacity of samples from several varieties was determined by first measuring the breaking load and weight fineness of the center section of fibers from each length group. These strengths were weighted in accordance with the length distribution of the cotton, and an "average tenacity" was calculated. If a more rapid method is desired for this determination, a characteristic index, bearing a fixed relation to this average tenacity, can be determined by testing only a few length groups. A method of calculating such an index is discussed, and its relation to the average tenacity is demonstrated.

The elongation at break of each fiber was recorded, and an average value was determined for every length group. These values were studied in relation to fiber length and strength.

The whole-fiber weight fineness and the coefficients of variation of breaking load and elongation for all length groups were also determined.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Experimental Procedure

Samples

A sample of cotton from each of these 6 varieties was studied: Sea Island, Egyptian Karnak, Acala 1517, Stoneville 2B, Rowden, and Half and Half. With the exception of the Sea Island sample, which was in the form of a roving, all samples were simply bulk cotton which had been ginned. These samples were chosen to represent a wide range in such physical properties as length, maturity, and whole-fiber fineness, as shown in Table I. These properties were determined by A.S.T.M. Standard test procedures [1].

The sample from each variety was sorted into $\frac{1}{32}$-in. intervals by the standard method for length arraying [1]. At least two arrays were made and the respective length groups were combined for each cotton in order to obtain samples that would be representative of each length group. The length group was then carefully blended by hand in order to ensure minimum variation among fiber bundles taken from it. From these samples, small bundles were removed, as needed, for measurements of other fiber properties.

All weighing and testing were done in an atmosphere of 65% ± 2% R.H. and 70° ± 1°F.

Method of Mounting Fibers

The method of mounting the fibers by cementing them across paper tabs was essentially that described in a previous publication [5]. The cement consists of a 10% solution of cellulose acetate in acetone, with diacetone alcohol added to prevent too rapid drying. The cement applicator is a 6-cm. length of 12-mm. glass tubing which at one end is drawn to an orifice about 0.007 mm. in diameter (see Figure 1). The cement is forced from the applicator by means of air under pressure,

TABLE I. PHYSICAL CHARACTERISTICS OF COTTON SAMPLES

	Sea Island	Egyptian Karnak	Acala 1517	Stoneville 2B	Rowden	Half and Half
(A) Length distribution by weight (%)						
Length group ($\frac{1}{32}$ in.)	(%)	(%)	(%)	(%)	(%)	(%)
33	1.33	—	—	—	—	—
31	6.04	—	—	—	—	—
29	10.36	0.29	—	—	—	—
27	14.16	6.86	—	—	—	—
25	13.98	14.47	1.19	0.34	—	—
23	8.11	17.18	7.22	4.37	—	—
21	7.44	15.34	15.51	12.54	5.93	—
19	7.15	11.34	19.36	22.84	19.88	—
17	5.22	7.92	13.28	23.66	27.80	1.40
15	4.57	5.71	10.17	11.51	18.21	14.51
13	4.00	4.51	7.18	7.23	10.29	27.14
11	2.90	3.43	5.17	4.29	6.29	26.27
9	3.51	3.57	4.59	3.77	3.76	14.87
7	3.69	2.91	3 84	3.08	2.47	7.51
5	3.16	3.07	4.81	3.17	2.07	4.06
<5	4.38	3.40	7.68	3.20	3.30	4.24
25% point* (in.)	1.69	1.48	1.24	1.21	1.13	0.83
Mean length (in.)	1.29	1.18	0.95	1.00	0.95	0.69
Coefficient of variation (%)	39.5	34.3	40.2	30.5	28.0	29.1
(B) Whole-fiber weight fineness, maturity, flat-bundle strength						
Whole-fiber weight fineness (grex)†	1.1	1.2	1.4	1.6	2.3	2.2
Maturity (%)	73	91	73	79	90	87
Flat-bundle strength (g./grex)‡	4.9	4.9	3.9	4.5	4.0	3.8

* By definition, 25% of the fibers by weight are longer than the values given.
† The grex unit is defined as 1 g. per 10,000 m., and is equivalent to 2.54 μg. per in., or 0.9 denier.
‡ For the tester used, 1 g./grex = 1.85 Pressley index.

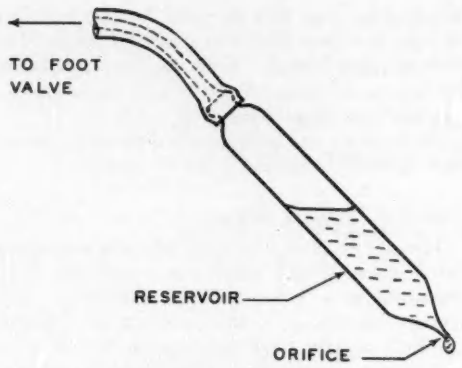

FIG. 1. *Cement applicator for mounting fibers.*

the pressure being controlled by a foot valve. When not in use, the orifice of the applicator is kept in acetone to prevent drying of the cement. After mounting, the cement is permitted to harden at least 24 hrs. before testing.

Description of Tester

Figure 2 is a schematic diagram of the single-fiber tester that was developed for performing the present experiments. The fiber to be tested is mounted between the pinch-clamp jaws, *E* and *F*. A micrometer adjustment of the lower jaw, *F*, makes it possible to accommodate different fiber specimen lengths. Force is applied to the fiber by the elongation of the spring, *B*; this is accomplished by means of the ladder chain, *H*, which is driven by the motor and gear combination, *D*.

The counter, *C*, which indicates the extension of the spring, is so geared to *D* as to read directly in tenths of a gram. To prevent overcoasting of the counter, which might otherwise occur after the fiber breaks, a magnetic brake (not shown in the diagram) is actuated by a sensitive switch which is closed by the upward movement of jaw *E* after the fiber breaks. This switch is actuated when any fiber breaks above 1-g. load. For fibers breaking at loads below 1 g., which is rare except in severely damaged cotton, an average strength of 0.7 g. is used.

The motor, *D*, is reversible, so that control of the tester is by a double-throw switch. Limit switches prevent overtravel in both directions, the lower limit being adjusted to return the counter to the zero-load position.

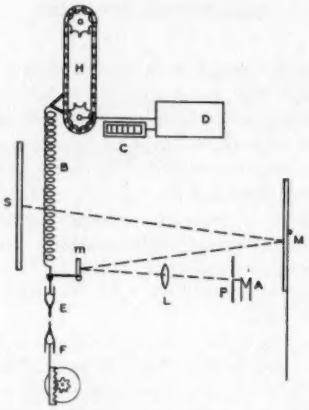

FIG. 2. *Single-fiber strength tester, showing specimen clamps,* E *and* F; *loading spring,* B; *chain,* H; *motor,* D; *counter,* C; *optical lever system,* m; *and elongation screen,* S.

Elongation is measured by means of an optical lever, *m*. Light from source *A* passes through lens *L*; an image of the cross-hair *P* is then produced on screen *S* by reflection from the optical lever, *m*, and the large mirror, *M*. The optical level is supported by means of pin bearings and a small ball-and-socket arrangement at the connection between jaw *E* and spring *B*. The elongation is magnified 50 × by this method. The elongation screen, *S*, is calibrated by raising jaw *E* in small increments, as measured by a microscope, and noting the deflection of the cross-hair image on *S*.

Various rates of loading are obtained by the gear box in combination with the motor. The following rates of loading are obtained with the 1-g.-per-cm. spring: 0.16, 0.32, 0.64, 1.23, and 2.50 g. per sec. To obtain the strength at any rate of loading between two settings, half of the samples are broken at the lower rate and half at the higher rate and the result is obtained by interpolation.

The constant for the spring used in single cotton fiber work is about 1 cm. per g. Therefore, in determining fiber strength a correction of 1.0 g. per cm. elongation of the fiber is made, to allow for the counter's registering the elongation of the spring as well as that of the fiber. This correction, which is in the neighborhood of 0.05 g. for cotton fibers, is subtracted from the average strength. It is considered negligible in calculations of variance.

Operating Procedure

The fiber is mounted in the jaws as for breaking, and a load of 0.2 g. is applied by rotating a convenient shaft of the gear box. This load is just sufficient to remove the kinks from most cotton fibers. At this time the exact specimen length is determined with a measuring microscope. Since specimen length is much less variable than either strength or elongation at break, measuring the length of 10 fibers per sample of 100 is sufficient to give a greater accuracy than that which is obtained in the other measurements.

Elongation is read beginning at the 0.2-g. load. The micrometer adjustment of the lower jaw is used in obtaining the zero-elongation setting at the beginning of each test. Since the stress-strain curve of cotton fibers under these conditions is nearly linear, it is possible to interpolate to zero load and obtain the total elongation. This correction is applied to the average. In practice, elongation must be read "on the run," because the cross-hair image disappears suddenly upon rupture of the fiber. Mirror *M* is adjustable about a horizontal axis in order to afford a fine adjustment of the elongation scale.

The breaking load and elongation of 100 fibers from each length group were tested as described above. The average rate of loading on these fibers was 1.0 g. per sec. Although the gap in the paper, across which the fiber was mounted, was cut to 6.35 mm. ($\frac{1}{4}$ in.), the actual corrected measurements of specimen length on 100 fibers, made as described above after removal of crimp and convolutions, averaged 7.14 mm. Elongation has been expressed as a percentage of this actual specimen length.

It was desired to test all length groups from the $\frac{5}{16}$-in. length to the longest in the sample in order to obtain a representative value of mean tenacity for the sample as a whole. Since the fibers in the $\frac{5}{16}$-in. group were too short to be tested at $\frac{1}{4}$-in. specimen length, a $\frac{1}{16}$-in. specimen length was used. The $\frac{7}{16}$-in. group was tested at specimen lengths of both $\frac{1}{4}$ and $\frac{1}{16}$ in. From these data and from the relationship reported to exist between tenacity and specimen length [3], the values for the $\frac{5}{16}$-in. length group at $\frac{1}{4}$-in. specimen length were calculated.

Determination of Fineness

Determination of an average value of single-fiber fineness on a bundle of fibers was satisfactory for this investigation and was more practical than individual-fiber tests. Fineness of the fibers was determined on the center section of the bundle because it was thought that this section would correspond more closely to the section tested for breaking load and elongation. For each length group a bundle of at least 100 fibers was inserted in a set of clamps, cut to a length of 1.2 cm., and weighed. The fibers were then counted and the fineness was calculated in grex. For length groups shorter than $\frac{9}{16}$ in., the weight fineness of the whole fiber was used.

Since the fibers had to be cut before weighing in order to determine their center fineness, and because fibers of this length would be difficult to mount, the same fibers were not used for strength and elongation tests. In order to introduce the least sampling difference between these bundles, both were taken from the same blended length group, as were all other bundles used in this study.

Experimental Results

Breaking load for individual fibers within a variety was found in general to increase with increased fiber length (Figure 3), although in some varieties it leveled off in the longer-length groups. The coarsest cottons, such as Rowden and Half and Half, had the highest breaking loads. The standard error of the mean of 100 observations averaged 0.24 g.; and the coefficient of variation ranged from about 60% for the shorter-length groups to 40% for the longer-length groups.

Weight fineness of the center section of the fibers varied with length and with variety (see Figure 4). In general, it increased with fiber length to a maximum value at a length slightly shorter than the modal-length group, and then decreased. (The modal-length group is the one containing the largest percentage of fiber by weight in the length distribution.) Half and Half showed the greatest change, Egyptian Karnak the least. The degree of precision of these values was estimated by determining weight fineness individually on 100 fibers of a length group from Acala and Rowden samples. Based on a coefficient of variation of 39%, the uncertainty of the mean at the 90% level was found to be about 6.5% in a normal distribution.

Within a variety, elongation at break of single fibers was also generally found to increase with increased fiber length (Table II). However, the

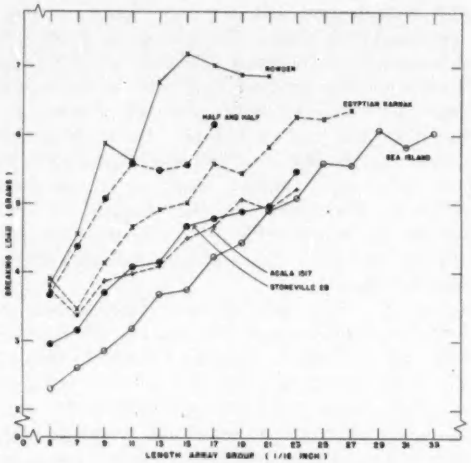

FIG. 3. *Relation of breaking load to fiber length.*

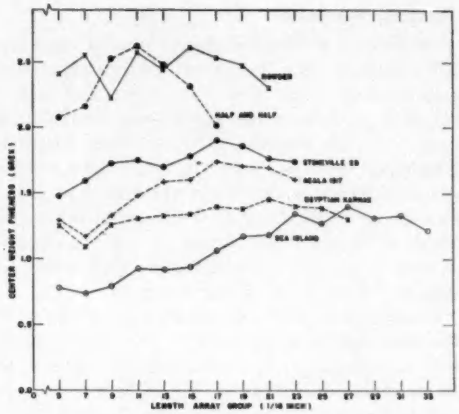

FIG. 4. *Relation of center weight fineness to fiber length.*

longest fibers of Egyptian Karnak and Sea Island cotton showed a decrease in elongation at break with increased fiber length, and there was no consistent change with length for Half and Half samples. Egyptian Karnak and Acala elongated more than the other samples, and Half and Half elongated the least. But elongation should be considered in proportion to the fiber strength (see Discussion of Results). The standard error of the mean elongation averaged about 0.37%, while the coefficients of variation ranged from about 50% for the shorter-length groups to 35% for the longer-length groups.

Discussion of Results

As shown in Figure 3, the coarser cottons had the higher breaking loads; the factor responsible for the higher breaking load is the greater size of the fiber. When the ratio of breaking load to weight fineness (tenacity or specific strength) was plotted against length group, the coarser cottons were found to be much weaker than the finer ones (see Figure 5).

In all varieties except Acala, tenacity showed a definite increase with increased length of fiber (Figure 5, showing data smoothed by the least-squares method [12]). In most cases the curve was S-shaped, with an inflection point occurring at a fiber length that was slightly shorter than the modal length. Acala, however, showed little change in tenacity; the shorter fibers had a higher tenacity in relation to the longer ones than was found in the other Upland samples.

As shown in Table II, elongation at break increases with fiber length. However, if the mean elongation for each length group is divided by the

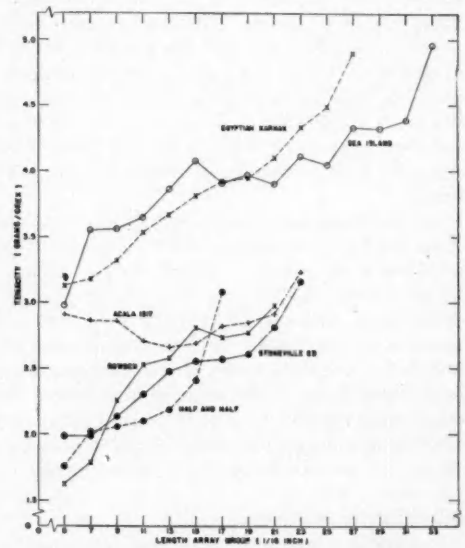

FIG. 5. *Relation of tenacity to fiber length.*

TABLE II. ELONGATION (%) AT BREAK OF SINGLE COTTON FIBERS

Length group ($\frac{1}{16}$ in.)	Sea Island (%)	Egyptian Karnak (%)	Acala 1517 (%)	Stoneville 2B (%)	Rowden (%)	Half and Half (%)
33	9.5	—	—	—	—	—
31	10.0	—	—	—	—	—
29	11.2	—	—	—	—	—
27	9.7	10.3	—	—	—	—
25	9.4	10.3	—	—	—	—
23	9.1	12.9	10.9	9.1	—	—
21	9.1	11.4	10.0	8.6	9.3	—
19	8.5	11.9	10.2	9.1	9.5	—
17	8.2	11.1	10.0	9.0	8.6	7.6
15	7.8	11.0	10.2	8.6	8.1	7.4
13	8.1	10.7	9.0	8.7	8.3	7.1
11	8.1	10.3	8.5	8.3	8.0	7.5
9	7.4	9.8	7.8	7.6	8.6	8.1
7	7.4	7.9	8.0	6.5	7.7	7.6
5	6.9	7.8	8.3	6.3	7.9	6.6

mean breaking load, the ratio decreases with increased fiber length for all 6 samples. Sea Island exhibited the greatest elongation per unit breaking load, Rowden and Half and Half the least.

Another method of relating strength to elongation is through the concept of stiffness. As defined by Smith [11], stiffness is the ability of a material to resist deformation; it is equal to the ratio of stress to strain. The "elastic stiffness" is equal to the slope of the initial, straight portion of the stress-strain curve; whereas the average stiffness is equal to the ratio at break of stress (specific strength or tenacity) to strain (extension per cm.). This average stiffness was calculated for each length group of the varieties tested, and was found to be the greatest for the sample of Sea Island and next greatest for Egyptian Karnak. The data did not indicate any consistent relationship between average stiffness and length of fiber within a variety—for some varieties the ratio increased, for others it remained the same or decreased. Among varieties there was a general relationship between fineness and stiffness, the finer varieties being the stiffer (see Table III). This is in agreement with the data given by Meredith [8] for 15 varieties of cotton.

The data on length distribution (Table I) and single-fiber tenacity were used to calculate an average tenacity for each of the 6 samples. These values were based upon the normal length distributions for the cottons, and were calculated by weighting the tenacity of each length group in accordance with the weight of the cotton of that length found to be present in the distribution. A sample calculation is given below. The average tenacity values of all length groups $\frac{5}{16}$ in. long and longer were used in this calculation; this represents about 96% of the total distribution. If the test were applied to a sliver or other processed sample, it would represent an even larger proportion of the distribution because many of the fibers shorter than $\frac{1}{4}$ in. are combed out in processing; also, those remaining contribute little of their strength to the total strength because of their shortness.

The comparison of cotton samples on a single-fiber basis is valuable in the evaluation of the mechanical properties of the samples. However, the testing of 100 fibers from each of these length groups, as described above, requires too much time to be practicable even in laboratory tests. If a few hundred fibers could be selected which would represent a large proportion of the distribution, a

TABLE III. AVERAGE STIFFNESS OF COTTON SAMPLES

Stiffness $\left(\frac{\text{g./grex}}{\text{strain}}\right)$	Sea Island	Egyptian Karnak	Acala 1517	Stoneville 2B	Rowden	Half and Half
	45	37	30	30	31	29

tenacity "index" could be calculated for the cotton from their tenacity values, which would still be characteristic of the sample. It was assumed that the means of 100 fibers from each of the 3 modal groups, weighted in accordance with their respective percent by weight in the length distribution, would be representative of the sample. The 3 modal groups for Stoneville 2B—the 3 consecutive groups containing the greatest percentage (by weight) of fiber in the length distribution—are listed below:

L Length group ($\frac{1}{16}$ in.)	T Tenacity (g./grex)	W Weight in length distribution (%)
21	2.81	12.54
19	2.63	22.84
17	2.52	23.66

The tenacity "index" was calculated in the following manner:

$$\text{Tenacity index} = \frac{\Sigma(W \times T)}{\Sigma W} = 2.62 \text{ g./grex.}$$

The average tenacity of the whole distribution was calculated in a similar manner, using all length groups from $\frac{5}{16}$ in. to the longest. For this specific sample a value of 2.56 g./grex was obtained. In Figure 6 is given a comparison of the average tenacity calculated on the whole length distribution with that calculated on only the 3 modal groups. When the tenacity index for the 6 varieties is plotted against the average tenacity of the whole distribution, the points fall nearly on a straight line (Figure 6). This line has a slope slightly greater than unity, as would be expected because the modal-group fibers are stronger than the average. The point of greatest departure from linearity is that for Acala, the uniformity in tenacity of which (see Figure 5) causes the point to fall nearer the line of unit slope.

This system of choosing fibers from definite length groups and weighting them in accordance with their occurrence in the sample should be more reliable and representative than the usual method of choosing an equal number of fibers randomly from the gross sample. Since the fibers of a comparatively large sample are sorted, the variable of length is practically eliminated, and the fiber bundles that are removed from the blended length groups represent fairly accurately the original large sample. Precision of the tenacity determination should therefore be increased, since tenacity is a function of length.

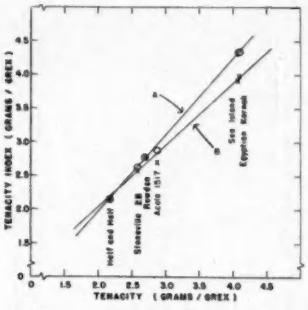

FIG. 6. *Relation of tenacity index based on 3 selected groups to tenacity of whole distribution.* A—*Modal groups.* B—*Mean-length groups.*

If, instead of using the 3 modal groups, indices are obtained using the mean-length group and its 2 adjacent length groups, correlation with whole-distribution values is less (see Figure 6). The 300 fibers tested by the modal-group method represent a larger percentage (40%–65%) of the total fiber weight than do those tested by the other method (20%–55%), except for the shortest cotton, in which case the modal and mean-length groups are the same.

In view of the dependence of the tensile and elastic properties of cotton fibers upon their position in the length distribution, specimens selected for testing should either represent the whole distribution or bear a constant relation to the whole distribution. Even in cases where treatments affect the length of fibers, the relative position of modal groups with respect to the whole distribution changes very little.

A comparison of results from the routine flat-bundle test with the average fiber strength as determined by the single-fiber method showed considerably less correlation than did either of the methods described above. This was to be expected since fiber properties other than strength are known to affect strength results in the bundle test.

Summary and Conclusions

From data obtained from single-fiber studies of length groups from American Upland cottons, the following conclusions were drawn:

1. The average breaking load and the average tenacity of single fibers increase with increasing fiber length within a sample.

2. Within a sample, weight fineness (taken on the center part of the fiber) reaches a maximum for fibers the length of which is near the modal length.

3. With increasing fiber length, elongation at break increases, ratio of elongation at break to breaking load decreases, and coefficients of variation for both breaking load and elongation at break decrease.

4. The finer varieties exhibit the greater average stiffness, or ratio of tenacity to strain.

5. A method is herein described for calculating a tenacity "index" for a cotton sample on the basis of single-fiber tests on only 3 length groups; this index shows a good correlation with the average single-fiber tenacity, which is calculated on the basis of all the fibers in the sample.

Acknowledgment

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Simple Expressions for the Circularity and Fullness of Fibers

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THE ROUNDNESS of cotton and other fibers has been shown to bear a relation to many fiber properties and characteristics, such as maturity [2], luster [1, 4, 10], resilience [13], mercerization [5, 6, 15], suitability for mercerization [10], breaking strength [7], and dyeing qualities [9]. One of the difficulties involved in establishing definite correlations, however, has been the lack of a sound method of designating shape by means of a simple function which can be used as a numerical index.

The methods employed up to the present time have admittedly been quite inadequate for general use. They include measurement of fiber width [5, 12] or ribbon width [3, 8], the relation between fiber width and wall thickness [10], the ratio of the cross-sectional area to the area of the circumscribed rectangle or circle [11], and the ratio of the major and minor "diameters," or axes, of the cross sections. The latter method is difficult to apply and a number of versions have been suggested [1, 18] for estimating the lengths of the axes in an effort to minimize the personal equation. All of these methods are purely empirical in nature, although some have proved very useful for specific purposes.

Schloemer [17], in connection with his considerations of rayon filaments, was the first to propose a sound mathematical basis for expressing fiber shape or roundness. He pointed out that when a fiber with a given periphery is filled to maximum theoretical capacity, its cross section will be perfectly round. This follows from the fact that a circle circumscribes the largest possible area for a given perimeter. He therefore defined fiber "fullness," or roundness, as the ratio of the area of the fiber cross section to the area of the circle of equal perimeter. This definition seems to have gone unnoticed except by Schwarz and Shapiro [18]. These investigators recognized its authenticity and used it in connection with their cotton-maturity studies (*a*) to correlate "circularity" (roundness) with their major-minor axis ratio, L/W, as obtained by their procedure; (*b*) to establish incidentally the degree of accuracy or reliability of their technique; and (*c*) to correlate the circularity and the L/W values with the maturity count as determined by the polarized-light color range method. They pointed out that if the cross section of the lumen had an appreciable area, an approximate correction could be made by calculating the circularity in the usual way and multiplying by the ratio $(LW - lw)/LW$, where L and l are the major and W and w are the minor axes of the fiber and the lumen cross sections, respectively, as measured by their technique.

It is the purpose of this paper to point out a number of interesting relationships and considerations which follow from Schloemer's concept and to show that it leads to very simple functions which can be used directly as indexes of the circularity and fullness of fiber cross sections.

The following symbols and definitions are used in the present study:

A = over-all area of the cross section

A_L = area of the lumen cross section

P = perimeter of the cross section

P_L = perimeter of the lumen cross section

$A_{(\max)}$ = area of the circle the perimeter of which is P

$A_{L(\max)}$ = area of circle the perimeter of which is P_L

r = radius of circle the perimeter of which is P

r_L = radius of circle the perimeter of which is P_L

C = circularity = $\dfrac{A}{A_{(\max)}}$, regardless of whether or not there are lumen or void spaces

F = fullness = $\dfrac{A - A_L}{A_{(\max)}}$

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The usual assumption is made that the cross section is taken normal to the axis of the fiber and that it is the same over the whole fiber length.

It will be noted that, according to the above definition, circularity, C, is a measure of the roundness of the outer contour of the fiber regardless of the amount of void or lumen space included. On the other hand, fullness, F, as the term implies, is a measure of the volume of substance (cellulose in the case of cotton) within the fiber as compared to the maximum volume it could contain and includes a correction for the void or lumen space. It is advantageous to so distinguish between these two terms since it is possible that some fiber properties—*e.g.*, luster—might be expected to show a correlation with circularity, while others—*e.g.*, maturity of cotton fiber—are manifestly related to fullness.

Circularity

From the above definition it is possible to derive a simple expression for the circularity in terms of A and P alone. Thus, since

$$A_{(\max)} = \pi r^2$$

and

$$P = 2\pi r,$$

by substitution,

$$A_{(\max)} = \frac{P^2}{4\pi} \tag{1}$$

and

$$C = \frac{A}{A_{(\max)}} = \frac{4\pi A}{P^2}. \tag{2}$$

The value of the function $\frac{4\pi A}{P^2}$, or $\frac{12.56A}{P^2}$, can thus be used as a measure of the circularity of any cross section regardless of its contour. It has already been found useful in investigations of the swelling of cotton in water [14] and of the orifice test for the closing capacity of cotton fibers in connection with the production of self-sealing, water-resistant fabrics [19]. This function may vary in value from unity, for a circle, to zero, for a cross section having a finite perimeter and zero area.

From equation (2) it is at once apparent that the circularities of two fiber cross sections having equal perimeters are directly proportional to their cross-sectional areas, or $\frac{C_1}{C_2} = \frac{A_1}{A_2}$; and that if they have equal cross-sectional areas their circularities are inversely proportional to the squares of their perimeters—*i.e.*, $\frac{C_1}{C_2} = \frac{P_2^2}{P_1^2}$.

Fullness

In connection with the fiber properties which are dependent upon the amount of substance within the fiber, such as maturity, the fullness should be determined, which takes into account the lumen or void space in the fiber. It is apparent from equation (1) that the fullness can be expressed as follows:

$$\text{Fullness} = \frac{4\pi(A - A_L)}{P^2}.$$

When A_L is zero the fullness equals the circularity.

The percent swelling is equal to the percent increase in fullness if the perimeter remains constant. If the perimeter is changed by the swelling treatment, the percent increase in fullness still equals the percent swelling if the initial perimeter of the fiber is used in calculating the fullness of the swollen fiber. This is also true if the original fiber is already partly swollen.

Error in Circularity Caused by Sectioning at Wrong Angle

In calculating the circularity of a fiber from the area and the perimeter of its cross section, the cross section must be made in a plane normal to the axis of the fiber. We shall refer to such cross sections as normal sections and to the plane as the normal plane.

For descriptive purposes let us suppose that the cross section is made by laying the individual fiber on a horizontal plane with the cutting *edge* perpendicular to the axis of the fiber and the cutting *plane* inclined at an angle θ from the normal plane. If the fiber is a right circular cylinder, the normal cross section is a circle of radius r and a circularity of unity. All other cross sections will be ellipses with semimajor axes a and semiminor axes b, where $a = \frac{r}{\cos\theta}$ and $b = r$. That is, as the angle θ is increased the minor axis will remain constant but the major axis will increase, and therefore the circularity of the cross section will decrease.

If the fiber is a right elliptical cylinder the normal cross section of which has a semimajor axis a' and a semiminor axis b', the cross section obtained for a given value of θ will depend upon the position of the

fiber on the horizontal plane. Only the two extreme positions will be considered—(case 1) those in which the fiber is lying on its more curved side (*i.e.*, the major axis of the normal cross section is perpendicular to the horizontal plane); and (case 2) the fiber is lying on its flatter side (*i.e.*, the minor axis of the normal cross section is perpendicular to the horizontal plane).

In case 1 all the cross sections obtained will be ellipses with semimajor axes a and semiminor axes b, where $a = \frac{a'}{\cos\theta}$ and $b = b'$. That is, as θ is increased the minor axis will remain constant and the major axis will increase continuously, and therefore the circularity of the cross section will decrease.

In case 2 ellipses will be obtained for all values of θ except that for which $\cos\theta = \frac{b'}{a'}$. For this particular value of θ, which we shall refer to as θ_1, a circular cross section will be obtained. As θ increases from zero to θ_1, the elliptical cross sections will have a constant semimajor axis and an increasing semiminor axis—*i.e.*, $a = a'$ and $b = \frac{b'}{\cos\theta}$—and therefore their circularity will increase to unity. Further increase in θ beyond θ_1 will result in a series of elliptical cross sections in which the semimajor axis increases and the semiminor axis remains constant, so that $a = \frac{b'}{\cos\theta}$ and $b = a'$, and therefore their circularities will decrease.

In order to determine the probable magnitude of this source of error on the calculated circularities for various values of θ, a preliminary analysis has been made of its effect on idealized fibers having normal cross sections which are either circular or elliptical, with semiaxes a' and b' such that $\frac{a'}{b'}$ equals 1.5, 3, and 10. In calculating the circularities of elliptical cross sections the following formulas [16] were used:

$$\text{Area of an ellipse} = \pi ab,$$
$$\text{Perimeter of an ellipse} = \pi(a + b)k,$$

where $k = 1 + \frac{1}{4}m^2 + \frac{1}{64}m^4 \ldots$ (neglecting all additional terms of the series) and

$$m = \frac{a - b}{a + b}.$$

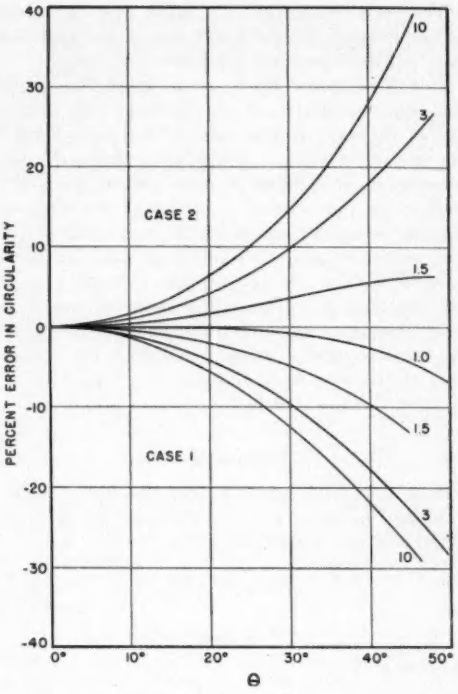

FIG. 1. *Error in circularity of cross section* vs. θ *for case 1 and case 2 when* $\frac{a'}{b'} = 1$ *(circle), 1.5, 3, and 10.*

The results are summarized in Figure 1, which shows the percent error in circularity involved as θ is increased for the various idealized fiber shapes. It will be noted that the error is very small for a circular fiber—*i.e.*, when $\frac{a'}{b'} = 1$. Thus, a deviation of 20° from the plane of the normal cross section results in an error of only 0.15% in the circularity and for a deviation of 30° the error is only 0.77%.

The magnitude of the error for a given value of θ increases as $\frac{a'}{b'}$ increases. When the fiber is cut in the manner of case 1, the error is always negative—*i.e.*, the calculated circularity is too low. For case 2 the error is positive for all values of $\frac{a'}{b'}$ considered in Figure 1. As mentioned in the general discussion of case 2, the error increases to a maximum and then

decreases. For $\frac{a'}{b'} = 1.5$ the maximum is reached when $\theta = 48.2°$. For $\frac{a'}{b'} = 1.05$ the error reaches a maximum when θ is about 18°, equals zero when θ is about 24.9°, and becomes negative for greater values of θ.

For values of θ up to about 20° the curves for case 2 are practically symmetrical with those for case 1. The maximum error shown is only 1.5% for $\theta = 10°$ and 6.5% for $\theta = 20°$.

In making cross sections experimentally, care is usually taken to parallelize the fibers in the fiber bundle as much as possible for imbedding so that sections inclined at more than 10° or 20° to the normal section should occur only in the case of individual fibers. It is thus apparent that the error in question is entirely negligible for circular fibers. As for the non-circular fibers, it is likely that approximately as many fibers would be cut in the manner of case 1, showing a negative error, as in the manner of case 2, showing a positive error, so that the resultant error for the whole bundle of fibers would tend to cancel out.

This analysis of the error caused by deviation of the cutting plane from the plane normal to the fiber axis can in no way be considered as applying quantitatively to cotton fibers with their variegated cross sections. However, perhaps it may be considered as a qualitative indication that the magnitude of the errors from this source is very small even for such fibers.

Summary

A simplified function, $\frac{4\pi A}{P^2}$, has been developed for designating the circularity of fiber cross sections, A being the area and P the perimeter of the cross section. A similar function has been derived to express the fullness of fibers.

An analysis has been made of the error caused by deviations of the cutting plane from the plane normal to the fiber axis in calculating the circularity of idealized fibers from cross sections. The probable experimental error involved is negligible for circular fibers. In the case of elliptical fibers with a ratio of major to minor axis as large as 10 the error would still be small and would tend to cancel out for a fiber bundle.

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The New Cover for *T. R. J.*

The change to white coated paper from the rough gray cover stock previously used for the cover of TEXTILE RESEARCH JOURNAL has been made so that the cover pages will be better suited for carrying advertisements, particularly where it is desired to reproduce halftones and colors. The spiralling costs of publishing make it all the more imperative that all possible economies be effected, and that an attempt be made to increase the income of the JOURNAL.

It is generally recognized that publication of the results of research is secondary in importance only to the actual research. Therefore, Textile Research Institute considers as one of its major services to the industry the publication of the JOURNAL, which requires a heavy subsidy on the part of the Institute. In order to allay expenses, an effort is being made to secure more advertising; also, it is believed that displaying in the JOURNAL advertisements of products and equipment appropriate to the interests of its readers will constitute an added service.

Front-Cover Design.—The fabric motif printed as a subdued background on the front cover of the JOURNAL is typical of a construction that could be made from any fiber, whether natural or man-made, and therefore it exemplifies the breadth of fiber interests of present-day textile research.

The 1950 *Journal*

Readers of TEXTILE RESEARCH JOURNAL have no doubt noticed the steady rate of increase in the number of pages from year to year. TEXTILE RESEARCH JOURNAL succeeded TEXTILE RESEARCH, the former publication of Textile Research Institute which had been restricted to members of the Institute. At present, the circulation to non-member subscribers outnumbers the circulation to members of the Institute and extends to 43 countries outside the United States and Canada. In 1945, the first year of the development of the new JOURNAL, 352 pages of research papers were carried and 133 pages of abstracts, a total of 485 pages. In 1949, there were 693 pages of papers and 165 pages of abstracts and book reviews, a total of 858 pages. Commencing with January, 1950, the abstracts section was omitted from the JOURNAL, and since then copies of the abstracts published by The Textile Institute of Great Britain have been distributed monthly to all of its subscribers, at no extra charge. These abstracts furnish a very complete coverage of the literature of the world as regards both textile science and textile development. It is impressive to note that the 1950 JOURNAL carried 856 pages of papers and 26 pages of book reviews. This represents an increase above 1949 in the number of pages devoted to research papers of 23½%, and an increase above 1945 of 143%. In addition, the abstracts mentioned above will comprise approximately 600 pages (the December issue has not reached us at the time of going to press).

In a series of articles describing world research organizations published in a British journal it was stated, "This publication (TEXTILE RESEARCH JOURNAL) has now attained the status of one of the most highly respected organs of the world for the publication of fundamental textile research work. It is, of course, not merely contributed to by Princeton (Textile Research Institute) workers but is supported by papers from many other laboratories, both inside and outside America."

Chemical Composition of Cotton

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ALTHOUGH CELLULOSE is the major constituent of raw cotton, any of the substances commonly found in plant cells may be expected to be present in at least small amounts. A recent literature survey [5] indicates that many investigators have reported typical values for one or more of the constituents present. These data are summarized in Table I to illustrate the composition of typical, mature cotton fiber. As very little attention has been given to the complete analysis of individual samples, the chemical composition of 6 samples of commercial raw cottons has been quantitatively investigated.

The physical properties of these cotton samples [1] are given in Table II. The sample of Empire cotton was from the 1944 crop grown on Cecil clay loam near Experiment, Georgia. That of Wilds was from a 1943 production near Stoneville, Mississippi. The Stoneville 2B sample was from the 1945 crop at Stoneville, Mississippi. The mature and immature cottons were of unknown variety. The contrast in the milling characteristics of these 2 cottons is reflected in the manufacturing waste, based on the net weight fed to the opener, of 8.21%, yarn grade of A −, and yarn strength (120-yd. skein break) of 329 lbs. for the mature sample, as compared to 17.45%, C, and 265 lbs., respectively, for the immature sample. The sixth sample was assumed to be of the Mebane variety. It was from a crop grown in 1941 at Big Springs, Texas. It had better than average spinning qualities.

The cottons were cleaned and blended, by use of standard textile mill equipment, prior to chemical analysis; thus, they were free of dirt, trash, and other foreign matter. The results of the analysis are given in Table III, and the results for the analysis of the ash of 2 of the samples are given in Table IV.

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In order to convert the analytical data to a dry-weight basis, moisture was determined as the loss on drying the sample in a forced draft oven at 105°C for 5 hrs. The cellulose content was evaluated by the monoethanolamine method [11]. The samples, which had been ground to pass a 20-mesh sieve, were extracted for 16 hrs. in a Soxhlet extractor in order to determine the water-extractables. The total sugars and reducing sugars were determined on a clarified aliquot of the water extract by using Somogyi's phosphate reagent [13]. Nitrogen was determined by a modified Kjeldahl method, using Nessler's reagent for the final evaluation [12]. The Conrad method [2] was used to evaluate the wax content. Samples were incinerated for 2 hrs. at 750°C for the determination of ash. Alkalinity of the ash was established by titrating with standard acid [3]. Citric, malic, and total organic acids were determined by the methods of Pucher *et al.* [9, 10]. The method of Whistler, Martin, and Harris [15] was employed for the determination of pectic substances. The constituents of the ash (Table IV) were determined by conventional wet-chemical methods.

The analytical data (Table III) show considerable variation in the chemical composition of the cottons. The variations in cellulose content reflect the loss in weight which occurs in kiering, bleaching, and other textile finishing operations in which most of the non-cellulosic constituents are removed. This loss appeared to be larger in the case of immature cottons.

The amount of total sugars and reducing sugars present is small, but significant variations are noted. If the conversion factor of 6.25 is assumed to be applicable, the values for nitrogen would indicate the presence of from 1% to 2% of protein. It has been indicated [12] that the yellow color of badly bleached cotton is associated with the protein content.

Considerable variation was found in the wax content. The wax is important as a lubricant of the

TABLE I. SELECTED VALUES FOR THE COMPOSITION OF TYPICAL, MATURE COTTON FIBER; DRY BASIS *

Constituent	Typical (%)	Low (%)	High (%)
Cellulose	94.0	88.0	96.0
Protein (N × 6.25)	1.3	1.1	1.9
Pectic substances	0.9	0.7	1.2
Ash	1.2	0.7	1.6
Wax	0.6	0.4	1.0
Malic, citric, and other organic acids	0.8	0.5	1.0
Total sugars	0.3		
Pigment	Trace		
Other	0.9		

* Moisture regain about 8%.

fibers in spinning. An inverse correlation between the wax content and maturity has been noted [7].

It has been pointed out [8] that there is a rough correlation between the content of organic acids and the ash and ash alkalinity. This is to be expected since the organic acids occur in the cotton fiber as salts. When the ash alkalinity exceeds the sum of the organic acids and pectic acid, both expressed as milliequivalents, the pH of the water extract is high. A similar correlation is observed between the water-extractables and the ash, except in the case of the immature sample.

Small amounts of oxalic acid have been isolated

TABLE II. PHYSICAL PROPERTIES OF COTTON SAMPLES *

Property	Empire	Wilds	Stoneville 2B	Unknown mature	Unknown immature	Unknown (probably Mebane)
Classer's Report						
Grade	SLM	SM		LM	MS	SLM
Staple (in.)	$1\frac{1}{32}$	$1\frac{1}{16}$		$\frac{29}{32}$	$\frac{13}{16}$	1
Length distribution						
Fibrograph						
Upper half mean (in.)	1.02	1.33	1.15	0.86	0.78	0.99
Uniformity ratio	70	71	73	80	74	78
Suter-Webb array						
Upper quartile (in.)	1.19	1.42	1.26	0.94	0.88	1.05
Mean length (in.)	0.96	1.14	1.04	0.79	0.66	0.90
Coefficient of variation (%)	32	34	29	28	43	26
Strength						
Pressley Index	6.0	8.8	7.4	6.1	6.0	6.2
Fineness						
Weight fineness (μg./in.)	4.1	3.0	4.0	5.6	3.6	5.0
Micronaire (scale units)	3.8	3.0	3.6	5.6	below 2	4.8
Maturity						
NaOH method	68	68	82	92	44	85

* Properties of unknown mature and unknown immature samples were determined on bale cotton; those of Empire, Stoneville 2B, and unknown (probably Mebane), on sliver lap; and those of Wilds, on roving.

TABLE III. ANALYSIS OF COTTONS; DRY BASIS

Constituent	Empire	Wilds	Stoneville 2B	Unknown mature	Unknown immature	Unknown (probably Mebane)
Cellulose (%)	95.30	93.42	95.58	96.41	92.44	94.93
Total sugars (%)	0.07	0.25	0.18	0.17	0.13	0.11
Reducing sugars (%)	0.01	0.17	0.04	0.02	0.03	0.02
Total nitrogen (%)	0.17	0.26	0.18	0.16	0.32	0.19
Wax (%)	0.73	1.07	0.69	0.45	1.14	0.57
Ash (%)	0.86	1.32	1.00	0.79	1.32	1.16
Ash alkalinity *	13.97	20.52	14.81	11.75	21.75	16.46
pH of the water extract	7.16	6.23	7.50	7.58	5.84	6.46
Water-extractables (%)	3.07	3.06	2.43	2.08	3.05	3.24
Organic acids *	8.20	13.67	7.88	5.77	14.56	12.87
Malic acid *	2.80	8.51	3.24	1.66	6.08	7.20
Citric acid *	0.66	1.45	0.74	0.58	1.49	0.86
Pectic acid *	5.6	6.9	4.8	3.2	7.0	4.7

* Milliequivalents per 100 g.

TABLE IV. ANALYSIS OF THE ASH OF 2 RAW COTTONS

Ash constituent	Unknown (probably Mebane) (%)	Empire (%)
K_2O	48.16	45.58
CaO	7.19	7.55
MgO	9.04	10.88
Na_2O	0.25	0.66
Fe_2O_3	0.20	0.36
Al_2O_3	0.31	0.73
SiO_2	0.76	0.75
SO_3	8.24	7.04
P_2O_5	4.22	4.40
Cl	1.22	2.12
CO_2	20.25	19.83
Total	99.84	99.90

from the fiber of the Empire cotton and from the sample of unknown variety [4]. Since the observed value for organic acids was larger than the sum of the individual acids which had been identified and determined, the presence of other acids was indicated.

A galacto-araban has recently been isolated and identified from several of these samples of cotton fiber, and indications of the presence of rhamnose and inositol have been reported [6].

The complete analysis of the ash (Table IV) from 2 of the cottons (Empire and the unknown variety) shows that potassium is the principal metal present. The ash also contains appreciable quantities of magnesium and calcium, and smaller amounts of sodium, iron, and aluminum. Acidic constituents present include carbonate, sulfate, phosphate, chloride, and silicate. The importance of ash constituents is indicated by the fact that washing cotton with water greatly increases its electrical resistance because most of the potassium and sodium salts are removed, making possible its use as insulation on telephone cord, wire, and cable [14].

Summary

The fiber properties of 6 samples of commercial raw cottons are tabulated, and the chemical analyses on them are reported for the following: cellulose, total sugars and reducing sugars, nitrogen, wax, ash, ash alkalinity, pH of the water extract, and the several organic acids present. The complete analysis of the ash of 2 of the cottons indicates that the principal metal present is potassium.

Acknowledgment

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Stabilization of Neutral Hypochlorite-Oxidized Cotton Fiber*

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Abstract

Cotton fiber oxidized by neutral hypochlorite solution, like cotton fiber oxidized by periodate, suffers two types of damage: one type is immediately evident; the other is latent damage, which becomes evident after exposure of the oxidized fiber to aqueous alkali. But when fiber oxidized by neutral hypochlorite is treated with ethereal diazomethane before exposure to alkali, a portion of the latent damage does not develop. The oxidized and treated fiber displays lower alkali solubility, lower cuprammonium fluidity, and greater strength after exposure to alkali than does the fiber that is oxidized but not treated.

Chlorous acid, found to be effective against the latent damage in periodate-oxidized cotton, is not effective against the latent damage in hypochlorite-oxidized cotton.

EARLIER WORK has shown that cotton fiber that is damaged by periodate oxidation responds to treatment with certain chemical reagents in such a way that the extent of damage is reduced. The beneficial effects of the post-oxidative treatments have been demonstrated by reduced cuprammonium fluidity, reduced alkali solubility, and greater strength after exposure to alkali [3, 4]. The two reagents that were found to be the most beneficial to periodate-oxidized fiber—chlorous acid and ethereal diazomethane—have now been applied to cotton fiber oxidized with neutral hypochlorite solution. Chlorous acid, the more effective of the two reagents against periodate damage, is without effect on hypochlorite-damaged cotton. On the other hand, ethereal diazomethane, the slightly less effective reagent, exhibits a definitely beneficial effect on neutral hypochlorite-oxidized cotton.

The different behavior of periodate- and hypochlorite-oxidized cotton with these reagents is undoubtedly a reflection of chemical differences between the two oxycelluloses. The reaction of chlorous acid with periodate oxycellulose has been attributed to the formation of carboxyl from aldehyde groups in the oxycellulose [2, 5]. The stabilizing action of diazomethane has never been adequately explained, but it is conceivable that this reagent reacts with aldehyde or ketone groups in periodate and in neutral-hypochlorite oxycellulose, respectively.

The present experiments, regarded as being of theoretical interest, demonstrate that latent damage (that which does not appear until after contact with aqueous alkali) can be reduced in hypochlorite as well as in periodate oxycellulose.

Experimental Methods

Sample Preparation and Oxidation

Mechanically cleaned raw cotton fiber (good middling grade, 1⅛-in. staple) was extracted successively with alcohol and water in a Soxhlet extractor and allowed to air-dry. The cuprammonium fluidity of this material was 1.65 rhes (reciprocal poise) in 0.5% concentration.

Samples of the extracted fiber were placed in 50 volumes of 0.1*N* sodium hypochlorite solution that had previously been buffered to pH 7.0 with a phosphate buffer. The oxidation was allowed to proceed in a thermostat at 25°C; samples were withdrawn after various lengths of time, rinsed with distilled water, and air-dried. This procedure

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produced samples ranging from mildly bleached to extensively damaged cotton fiber.

Diazomethane Treatment

Portions of various air-dried, oxidized fibers and an unoxidized control were treated with 60 parts of 0.42*M* ethereal diazomethane (from nitrosomethylurea) and allowed to react for 5 days at approximately 5°C. The samples were rinsed free of reagent with alcohol containing acetic acid and then with distilled water, and were air-dried. All methylated samples contained 5 ± 0.3% methoxyl, as determined by the micro Zeisel procedure.

Chlorous Acid Treatment

Portions of various oxidized samples and an unoxidized control were treated at 60°C for 1 hr. with 40 volumes of a solution containing 2% sodium chloride that had been buffered to an acidity of approximately pH 4 with potassium acid phthalate. These samples were rinsed with distilled water and air-dried.

Measurements

Alkali-solubility determinations were made by heating portions of the various fiber samples with 100 parts of 0.1% sodium hydroxide solution in a boiling water bath for 1 hr. The insoluble residues were filtered on sintered glass crucibles, rinsed with distilled water, and air-dried. The loss-of-weight values are expressed on an air-dry basis. These samples were reserved for cuprammonium fluidity and strength measurements.

Cuprammonium fluidity measurements were made at 25°C with 0.5% dispersions of anhydrous fiber in modified Clibbens and Geake viscometers [1]. The cuprammonium solution contained 15 g. copper, 240 g. ammonia, and 1 g. sucrose per l.

Strength measurements were made on a standard Pressley fiber-bundle tester. Since this tester gives results in terms of lbs. of breaking load per mg. of fiber (cut to a particular length), the data were recalculated to allow for weight changes during the processing treatments. Thus, in diazomethane-treated, alkali-extracted samples allowance was made for increase in weight due to partial methylation and for loss of weight due to alkali extraction. By this means the strength measurements were all related to equivalent amounts of the original cotton fiber.

Discussion of Results

The cuprammonium fluidity data on the various series of samples are presented in Table I and in Figure 1. Figure 1*A* shows that neutral hypochlorite-oxidized cotton fiber suffers two types of damage: (1) an immediately evident increase in cuprammonium fluidity; and (2) a labile condition which results in a further increase in fluidity on treatment with hot aqueous alkali. Figure 1*B* shows that a chlorous acid treatment following oxidation does not reduce either of these types of damage. Figure 1*C* illustrates the beneficial effects of a diazomethane treatment following oxidation—not only are the immediate fluidity values slightly decreased, but also the alkali-labile condition is completely stabilized as far as fluidity is concerned. The diazomethane-treated samples do not exhibit a further increase in fluidity on alkaline treatment.

The fiber strength data are presented in Table II and in Figures 2 and 3. The table gives the Pressley strength values after adjustment to allow for weight changes in the fiber during treatment. In the figures the strength values for each series of samples are related to the strength of the series control, the latter strength being taken as 100%. Again, the dual nature of the damage caused by neutral-hypochlorite oxidation is apparent. In Figure 2 the stippled area represents strength loss due to oxidation alone; the lined area, the further loss of strength due to subsequent exposure of the oxidized sample to hot aqueous alkali. Figure 3 illustrates the protective action of diazomethane against the second type of fiber damage. The stippled area represents strength loss due to oxidation alone; the lined area, the further loss when diazomethane treatment precedes the alkali treatment; and the dark area, the extent of the beneficial effect that is attributable to the diazomethane treatment. This amounts to 10%–15% of the original fiber strength throughout most of the oxidized region.

When chlorous acid treatment was substituted for the diazomethane treatment, no appreciable differences were noted between the strength of the oxidized and the oxidized, chlorous acid-treated samples after exposure to alkali.

The amount of fiber that is soluble in hot dilute sodium hydroxide is listed in Table III for samples in each series: oxidized only; oxidized, chlorous acid-treated; and oxidized, diazomethane-treated. It is

TABLE I. CUPRAMMONIUM FLUIDITIES OF OXIDIZED; OXIDIZED, CHLOROUS ACID-TREATED; AND OXIDIZED, DIAZOMETHANE-TREATED CELLULOSE

Time of oxidation (min.)	Oxidized only		Oxidized, chlorous acid		Oxidized, diazomethane	
	Before alkali (rhes)	After alkali (rhes)	Before alkali (rhes)	After alkali (rhes)	Before alkali (rhes)	After alkali (rhes)
0 (control)	1.65	1.91	1.93	2.27	2.21	2.40
10	8.8	20.5	10.1	20.2	6.66	6.47
26	14.5	31.3	15.1	28.6	—	—
30	15.2	30.7	—	—	14.3	12.4
105	29.3	41.7	—	—	26.3	26.3
120	28.8	46.1	32.8	44.4	—	—
220	40.5	50.2	—	—	36.4	36.5
240	42.0	50.5	41.0	49.5	—	—
1180	51.0	—	—	—	48.3	48.3

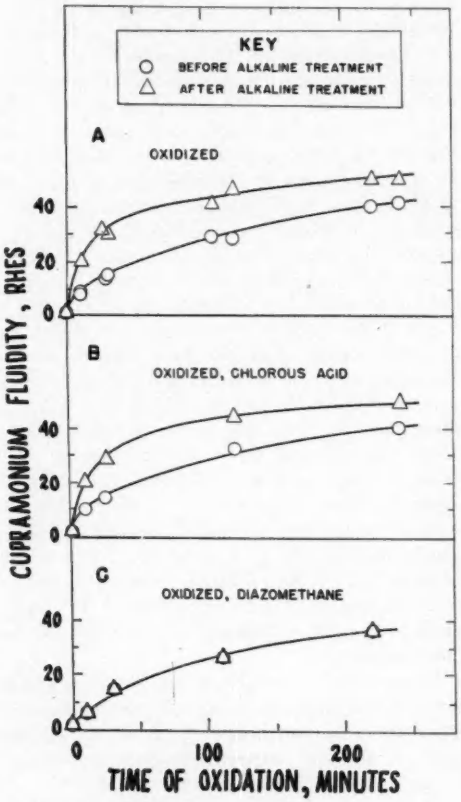

FIG. 1. *The cuprammonium fluidity of* (A) *oxidized;* (B) *oxidized, chlorous acid-treated; and* (C) *oxidized, diazomethane-treated cotton fiber before and after exposure to hot aqueous alkali.*

TABLE II. FIBER STRENGTH MEASUREMENTS OF THE OXIDIZED; OXIDIZED, ALKALI-TREATED; AND OXIDIZED, DIAZOMETHANE-, ALKALI-TREATED SAMPLES

Time of oxidation (min.)	Oxidized only* (lbs./mg.)	Oxidized, alkali† (lbs./mg.)	Oxidized, diazomethane, alkali‡ (lbs./mg.)
0 (control)	5.86	6.20	6.04
10	5.78	5.15	5.55
30	5.55	3.91	4.68
105	4.56	2.83	3.17
220	3.47	1.56	2.14

* Pressley fiber-bundle strength.

† Pressley value adjusted for loss of weight due to alkali treatment.

‡ Pressley value adjusted for gain in weight due to partial methylation and loss of weight due to alkali treatment.

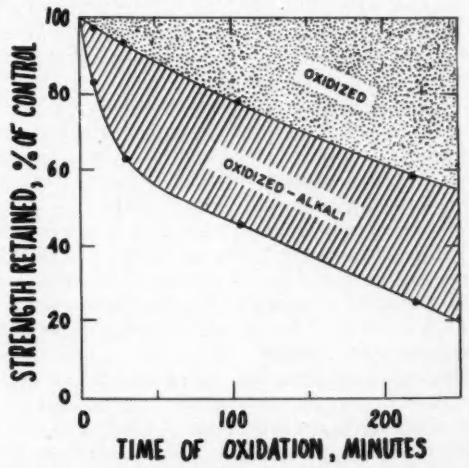

FIG. 2. *Strength retained at various extents of oxidation before and after exposure to hot aqueous alkali.*

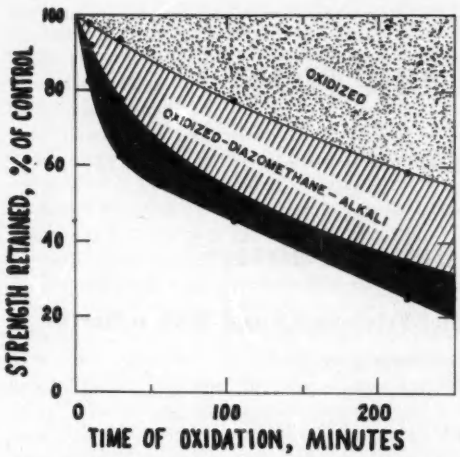

FIG. 3. *Strength retained by oxidized, diazomethane-treated cotton fiber after exposure to hot aqueous alkali. The dark area represents the beneficial effect of the diazomethane treatment.*

apparent that chlorous acid was without effect on alkali solubility, while at the higher levels of oxidation diazomethane very markedly reduced the amount of alkali-soluble material.

Quantitatively, only a small amount of protection against ultimate loss of strength is afforded by the action of ethereal diazomethane on neutral hypochlorite-oxidized cotton fiber. However, the treatment definitely lowers the cuprammonium fluidity of the oxidized fiber and stabilizes it against the action of alkali. At the higher levels of oxidation it markedly decreases alkali solubility. Ethereal diazomethane is a slow, expensive, and unwieldy reagent for this purpose, but its use demonstrates that hypochlorite as well as periodate damage may be reduced by appropriate chemical treatment.

TABLE III. ALKALI SOLUBILITY OF OXIDIZED; OXIDIZED, CHLOROUS ACID-TREATED; AND OXIDIZED, DIAZOMETHANE-TREATED CELLULOSES

Time of oxidation (min.)	Oxidized only (%)	Oxidized, chlorous acid (%)	Oxidized, diazomethane (%)
0 (control)	1.6	2.3	1.3
10	2.6	3.1	1.4
26	3.6	3.7	—
30	4.0	—	1.3
105	7.1	—	2.0
120	5.6	5.7	—
220	10.4	—	2.6
240	7.7	6.8	—
1180	42.1	—	6.9

Acknowledgment

The authors are indebted to W. S. Smith, W. A. Posey, Annie B. Cooper, and Dorothy C. Legendre for Pressley strength measurements made during the course of this work.

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INDUSTRIAL SECTION

The Rate of Drying of Fabrics*

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Abstract

It is frequently stated that one fabric dries faster than another, usually with reference to household conditions of drying on a line. However, the data of this report show that by and large all fabrics dry at the same rate under these conditions (rate being expressed as weight of water evaporating per unit area per unit time), but that the time of drying depends upon the amount of water originally held, so that some fabrics dry sooner than others. The main portion of the drying time shows this constant rate of drying, although there is a final period which is short compared to the main drying period, during which the rate of drying decreases.

The water-holding capacity of a fabric depends upon how the fabric is supported (vertically or horizontally) and upon the mechanical treatment given to remove water. For simple drainage in the vertical position, the water-holding capacity of small samples is more closely correlated with fabric thickness than with fabric weight. The kind of fiber—*i.e.*, wool or cotton—and large differences in moisture affinity, as shown with Vinyon, also affect the water-holding capacity. However, these factors have almost no effect on rate of drying, since this is controlled by the resistance of air layers to the passage of heat. The thickness of these air layers is sufficient under ordinary conditions to smooth-over the fabric surface irregularities, even when these are rather large, as in rib knits or in cellular or waffle fabrics.

Increasing the hairiness of the surface in order to give more area for evaporation is sometimes proposed as a means of increasing the drying rate, but results show that this is without effect except for extremely high, open naps, for which the effect is the opposite—the thickness of the layers of still air is increased and the drying retarded.

STANDARD REFERENCES on engineering [1, 3] and publications in the literature of textile drying [4] point out that the course of drying is divided into stages, and that a "constant-rate period continues as long as the water in the material comes to the surface so rapidly that the surface remains thoroughly wet, and evaporation proceeds at a constant rate, precisely as from a free water surface" [1]. The point in the drying process at which the rate of drying ceases to be constant is known as the "critical moisture content" [1, 4]. In the general case [1] this constant-rate period is followed by one of falling rate, in which a decreasing fraction of the surface is saturated or in which the drying takes place below the surface. Preston and Chen [4] regard the critical moisture content for textiles as being equivalent to the regain of the textile in equilibrium with an atmosphere of 100% relative humidity, although recognizing that this quantity has seldom been precisely determined. This

* This work began in the Research Fellowship of the Textile Foundation at the National Bureau of Standards, under Contract W950-QM-4674 with the Quartermaster Corps on thermal transmission of moist fabrics and Contract OEM-cmr-304 with the Office of Scientific Research and Development on comfort in clothing, and additional work has been done at the Harris Research Laboratories.

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implies that for textiles the adsorption of water by the fabric substances is the rate-changing influence rather than mechanical or geometrical effects such as partial surface wetness or increased resistance in subsurface drying.

In view of the authoritative recognition of the "approximate fact" of the constant drying rate for removal of liquid (nonbound, nonabsorbed) water from thin layers of porous materials, it is surprising how often not only the "man in the street" but also workers in the textile field speak of differences in drying rate and expect to produce differences in fabrics by choice of fiber or features of cloth structure. The purpose of this report is to inquire into the range of validity of the constant-rate generalization, and into the basis of the "common sense" idea of varying rates. This has lead to a study of the influence of structural factors on water-holding capacity, and of the thickness of the air films which govern transfer of water vapor away from, and of heat toward, fabrics during drying.

Methods

The experiments were made with square pieces of fabric cut 5 in. on edge. These were wet-out by soaking overnight in distilled water. The saturated specimens were suspended, with edges in either the horizontal or the vertical position, and were allowed to drain until only 1 or 2 drops of water dripped per min. The weight under these conditions was taken as the maximum water content for simple drainage. The specimens were then hung on the rim of a slowly revolving wheel, or were changed in position on a line, so that conditions of air movement and exposure to radiation would be equalized. The course of the drying process was followed by weighing the samples at intervals. The conditioned weight after drying was taken as the base. All rates were determined in the A.S.T.M. standard textile testing atmosphere—65% R.H., 70°F—but conditions of air movement varied in the different series of experiments.

Fabric thicknesses were measured by means of the compressometer [5], except at the lowest pressure—0.026 g./cm.²—which was used in order to obtain measurements that would be more characteristic of the free-standing thickness of hairy fabrics. These measurements were made by focusing a microscope, with 20 × objective, on marks on the surface of a glass cover slip. A dial indicator attached to the microscope measured the vertical displacement between points of focus when the cover slip rested on the stage and on the surface of the fabric.

Results and Discussion

Drying Rates per Unit Area or per Unit Weight

Drying curves for group *A*, a set of knit underwear fabrics and blankets, are shown in Figures 1 and 2. Curves showing grams of water remaining per gram of fabric (equivalent to curves giving % water content), as in Figure 1, are widely divergent, and may be in part a basis for the idea of different drying rates for different fabrics, especially among technical workers. However, when the weight of water remaining per unit area of fabric surface is plotted, as in Figure 2, so that the rate of change represents the loss of water per unit of surface, all the fabrics are brought together at a substantially constant rate. Hence, unless otherwise specified, throughout this report drying rates are expressed in terms of water loss per unit area and unit time. The surface area is somewhat more than twice the area of the fabric as ordinarily measured, since with the thicker fabrics the area of the edges becomes appreciable. However, unless otherwise indicated, the surface area is taken as twice the cloth area.

Transition from Removal of Liquid to Adsorbed Water

The lines of Figure 1 begin to curve at water contents between 20% and 10% of the conditioned (base) weight. For wool, the regain at 65% R.H. is roughly 16% and at saturation 36% [4]; therefore, (20/116) × 100 = 17%, on the conditioned weight, is the transition between adsorbed and liquid water. A similar calculation for cotton gives 10%. Thus, these experiments are in general agreement with those of Preston and Chen [4] as to the identity of the critical water content with saturation equilibrium.

Range of Constancy of Drying Rates

In Figure 2, the bunching-together of points showing the amount of moisture on an area basis suggests that the rate of drying for these fabrics is substantially constant. In fact, a plot of rate against thickness shows only a scattering around an average, with no definite trend. The same examination has been made for other groups of

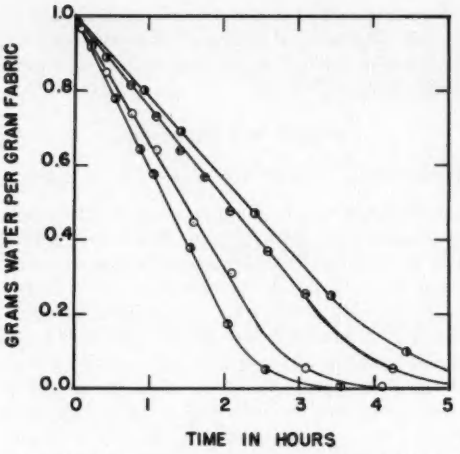

FIG. 1. *Drying curves, on the basis of water content per unit weight of fabric, for cotton and wool underwear fabrics and a wool blanket, ranging from 1.07 to 2.51 mm. in thickness and from 35 to 56 mg./cm.² in weight.*

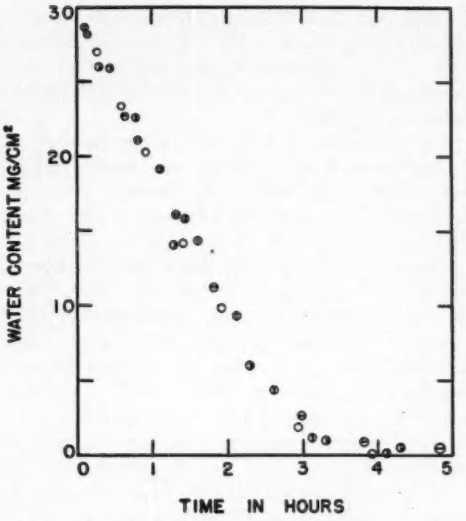

FIG. 2. *Drying plots, on the basis of water content per unit area of fabric surface, for the fabrics of Figure 1. All observations are substantially on the same line.*

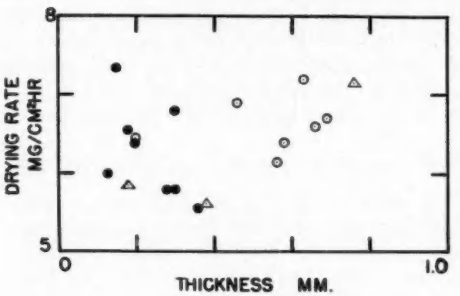

FIG. 3. *Drying rates for the thin fabrics described in Table I. Open circles indicate solidly woven cotton fabrics; triangles indicate special, more open-weave cottons; filled-in circles indicate continuous-filament synthetic fabrics. Thickness is measured at 7 g./cm.² pressure.*

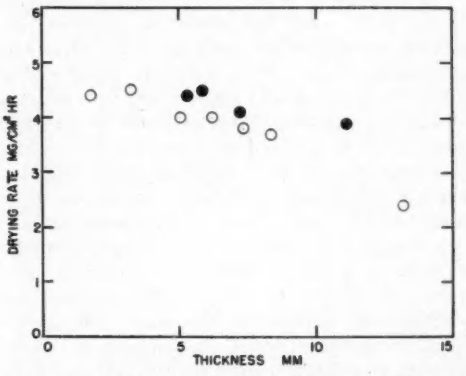

FIG. 4. *Drying rates for the thicker wool fabrics described in Table II. Open circles indicate woven or knit fabrics; filled-in circles indicate felts. Drying rates have been corrected for the area of the edges, based on the thicknesses at 0.026 g./cm.² pressure, which are the thicknesses shown.*

fabrics, each group being tested under constant conditions, except for variations of exposure conditions from one group to another, which are reflected in shifts of the general rate level for the different sets.

Figure 3 shows the drying rates for group *B* fabrics—solidly woven cotton fabrics, some special open-weave cottons, and some compact fabrics made of continuous-filament yarns. For these also there is no variation of rate with thickness, although it should be noted that all of these are thin fabrics with smooth surfaces. Descriptions and measurements of these fabrics are given in Table I.

To extend the results to very thick fabrics, group *C* fabrics were studied. This group contains both

TABLE I. PROPERTIES OF COTTON FABRICS AND OF CONTINUOUS-FILAMENT FABRICS (GROUP *B*)

Description	Thickness* (mm.)	Weight (mg./cm.²)	Maximum absorption (mg./cm.²)	Water held / Cloth weight	Rate of drying (mg./cm.² hr.)
Solidly woven, smooth cottons					
Balloon cloth	0.20	7.3	9.1	1.25	6.5
Poplin (civilian shirting)	.30	11.1	15.0	1.35	—
Sheet	.38	14.8	19.5	1.32	—
Oxford cloth shirting	.43	12.5	23.4	1.87	—
Byrd cloth, twill	.46	20.8	19.2	.92	6.9
Poplin (Army shirting), 5-oz.	.56	22.6	21.5	.95	6.2
Khaki twill, 6-oz.	.58	19.5	27.6	1.42	6.4
Herringbone twill, A	.61	27.8	29.9	1.08	—
Uniform twill, 8.2-oz., A	.61	31.0	28.4	.92	—
Sateen, 5-harness, 9-oz.	.63	33.0	25.7	.78	7.2
Uniform twill, 8.2-oz., B	.76	33.2	32.5	.98	6.6
Herringbone twill, B	.79	30.9	35.4	1.14	6.7
Other cotton fabrics					
Mosquito net (Ceglin finish)	.28	5.7	9.0	1.58	5.8
Absorbent gauze	.38	3.3	10.2	3.10	5.6
Cellular cloth	.76	27.8	32.5	1.17	7.1
Knit undershirt	.79	15.9	46.1	2.90	—
Hand towel	1.27	29.2	63.6	2.18	—
Flannel	1.65	15.9	116.9	7.35	—
Terry cloth	3.00	44.5	147.8	3.32	—
Continuous-filament fabrics					
Nylon A	.20	11.5	6.9	0.60	6.4
Nylon B	.30	15.4	9.2	0.60	6.8
Plain-weave Vinyon					
Light sailcloth	.18	12.0	4.6	0.38	6.5
Intermediate sailcloth	.28	18.4	6.1	0.33	—
Experimental uniform fabric	.36	13.5	8.2	0.61	5.5
Heavy sailcloth	.56	30.6	11.0	0.36	—
Filter fabric	.74	45.2	14.1	0.31	—

* Thickness is measured at a pressure of 7 g./cm.².

TABLE II. PROPERTIES OF WOOL FABRICS (GROUP *C*)

Description	Thickness at 0.026 g./cm.² pressure (mm.)	Thickness at 7 g./cm.² pressure (mm.)	Weight (mg./cm.²)	Maximum absorption (mg./cm.²)	Water held / Cloth weight	Rate of drying (mg./cm.² hr.)	Corrected rate of drying (mg./cm.² hr.)
Felts							
Silence cloth felt	5.3	2.53	36.5	175	4.80	4.7	4.4
Mukluk felt	5.85	4.41	110	306	2.75	4.9	4.5
Sole felt	7.2	5.29	129	374	2.90	4.5	4.1
Mukluk felt	11.1	8.97	300	540	1.80	4.6	3.9
Knit or woven fabrics							
Tropical worsted	1.78	0.67	24.9	33	1.33	4.5	4.4
Covert, all wool, U. S. Army	2.62	1.33	34.2	77	2.25	4.7	4.5
Army blanket, No. 1	5.03	2.41	52.5	118	2.25	4.3	4.0
Army blanket, No. 2	7.34	4.02	59.7	200	3.35	4.2	3.8
Felted knit outerwear	6.20	4.11	66.9	254	3.80	4.4	4.0
Civilian blanket	8.39	4.35	43.3	175	4.05	4.2	3.7
Papermaker's "felt" (Yankee, bottom)	13.16	6.84	72	127	1.76	3.0	2.4

rather solid, uniformly structured felts and less solid, more hairy woven and knit structures. When the drying rates of this series are based on twice the cloth area, the rates are remarkably constant; when correction is made for the additional area of the edges, the rate is still nearly constant, but shows

a small tendency to fall-off with increasing thickness, as can be seen in Figure 4. The properties of group *C* fabrics are listed in Table II.

One fabric shows a drying rate lower than all the others. This is a highly napped, blanket-like fabric, actually a papermaker's Yankee bottom felt. It is of special interest because it indicates that increased hairiness, which has sometimes been advocated as a means of increasing the evaporative surface, can be a step in the wrong direction.

Drying-rate data have also been obtained on knit underwear fabrics, covering a wide variety of styles of knitting and blends of wool and cotton. The structures of these fabrics are shown in another publication [2]. The thicknesses range from 0.6 to 3.8 mm., without any marked trend of rate of drying.

Air Films Rather than Fabric Structure as Determiners of Drying Rate

The data show that at least up to over 10 mm., or nearly ½-in. fabric thickness, the rate of drying for exposure on a line is constant, almost independent of fabric thickness or structure, except that unusual hairiness of an open texture may retard the drying. This is compatible with the view that the factor governing the rate of drying is the rate of diffusion of water vapor away from the fabric, or of heat towards it, through layers of relatively still air.

The thickness of the air film which controls the drying rate can be calculated, with either heat flow or vapor diffusion as the controlling factor.

For the calculation of resistance to heat flow, the temperature difference is needed. This was determined by thermocouples on the surface and in the interior of fabrics, with simultaneous measurements of dry- and wet-bulb temperatures. The results for several fabrics are shown in Table III, and indicate a temperature difference of 2.8°C under these conditions, which is the same for different types of fabrics.

TABLE III. AVERAGE TEMPERATURES DURING TWO CYCLES OF ROOM CONDITIONS

Material	T_A Dry bulb (°C)	T_W Wet bulb (°C)	T_C Cloth (°C)	$T_A - T_C$ (°C)
Khaki, 6-oz.	20.79	16.66	17.92	2.87
Poplin, 5-oz.	20.79	16.65	17.98	2.81
Blanket, interior	20.71	16.62	18.00	2.71
Blanket, surface	20.69	16.62	17.92	2.77

The calculations of air-film thickness for heat flow take the form:

$$\text{Film thickness} = \frac{\text{temperature difference}}{\text{rate of flow of heat}} \times (\text{thermal conductivity of air}).$$

The drying rate in these trials was 6.35 mg./cm.² hr., which requires 10.3×10^{-4} g.cal./cm.² sec. as the rate of flow of heat in order to maintain a steady temperature. This inward flow is by two mechanisms—one is the absorption of radiant energy, and the other is the conduction through the film of air lying between the fabric and the general atmosphere. The flow of heat by radiation can be calculated by the Stephan-Boltzmann law:

$$H_R = S\, e_1\, e_2\, (T_1^4 - T_2^4)\, A,$$

where H_R = heat flow by radiation; S = Stephan-Boltzmann constant = 1.37×10^{-12} g.cal./cm.² sec.; e_1, e_2 = emissivities of fabric and surroundings, taken as unity; T = absolute temperature; A = area.

For the observed room and cloth temperatures, H_R is 3.8×10^{-4} g.cal./cm.² sec., leaving 6.5×10^{-4} g.cal./cm.² sec. to flow through the air film. Using the thermal conductivity of air given in International Critical Tables, the air film governing heat flow is found to be 2.4 mm. thick.

The corresponding calculation for the air film which would limit diffusion of water vapor to the observed rate is made by the equation:

$$R = \frac{1}{Q} D\, (C_1 - C_2)\, A\, t,$$

where R = thickness of air film in cm.; Q = weight of water vapor diffusing in g.; D = diffusion constant; C = concentration of water vapor in g./cm.³ at fabric surface or in general environment; A = area in cm.²; t = time in sec.

The thickness of the air film for the conditions of these measurements is 4.6 mm. if vapor diffusion is considered to be the limiting factor. Comparison of the two calculated film thicknesses shows that the limiting factor is flow of heat, since the required amount of heat could not flow through the film thickness which would limit vapor diffusion, while even more water vapor than does can pass through the film which limits heat.

While the thickness of a fabric, as usually determined under a specified pressure, is less than the

effective thickness of the free-standing fabric, it is clear that the 2.4 mm. air-film thickness is greater than the total thickness of many fabrics, and is great enough to smooth out the effect of all save the largest surface irregularities, even in fabrics of total thickness greater than 2.4 mm.

Water-Holding Capacity as Determiner of Drying Time

Since the drying rate for fabrics suspended on a line is practically constant over a wide range of fabric structures and thicknesses, differences in rate cannot explain the well-known differences in time required to dry. Except for the last phase of drying—the removal of adsorbed water—the time to dry must depend upon the fabric water content at the start of the drying period. While in practice this will depend upon the effectiveness of the mechanical removal of water, as by wringing or spinning, the limiting case is the maximum water content without dripping, which has been determined for many of the fabrics studied. Trials of mechanical wringing show that a typical wringer reduces the water content to between 90% and 60% of the fabric weight; hence, the major portion of the practical drying time is concerned with the removal of liquid water.

The maximum water content can be expected to be related to either fabric weight or fabric thickness. The correlation with thickness is the more regular of the two, and is shown in Figure 5 for the cotton, Vinyon, and nylon fabrics of group *B* and in Figure 6 for the wool fabrics of group *C*. The thicknesses shown were all measured at 7 g./cm.^{2} pressure, equal to 0.1 lb./in.^{2} or 130 lbs. per sq. yd. This pressure is large compared with fabric weights, and presses the surface hairs or nap of most of the fabrics into a compact, relatively uniform mass. This is shown by the fact that the woven or knit wools, and especially the blankets, fall on the same line (Figure 6) as the compact, uniform felts.

If the thickness of the wool fabrics is measured at a much lower pressure, 0.026 g./cm.^{2}, a rather different picture is obtained, as shown in Figure 7. Here the compact woven and knitted fabrics and the felts still fall on a common line, but the napped fabrics hold less water relative to their thickness. These are the fabrics which showed the greatest

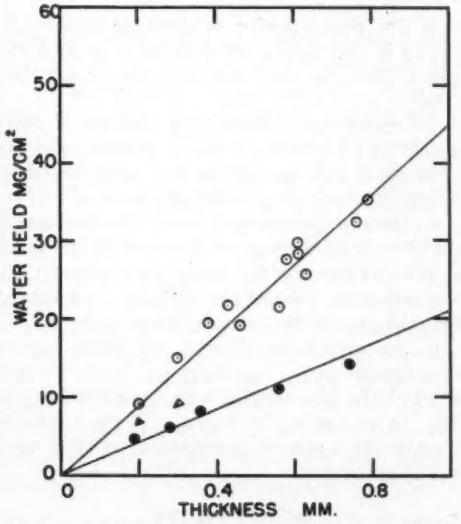

FIG. 5. *Relation between maximum water-holding capacity and thickness, as measured at 7 g./cm.^{2} pressure. Solidly woven cotton fabrics are indicated by open circles; plain-weave filament Vinyon fabrics by filled-in circles; filament nylon fabrics by triangles.*

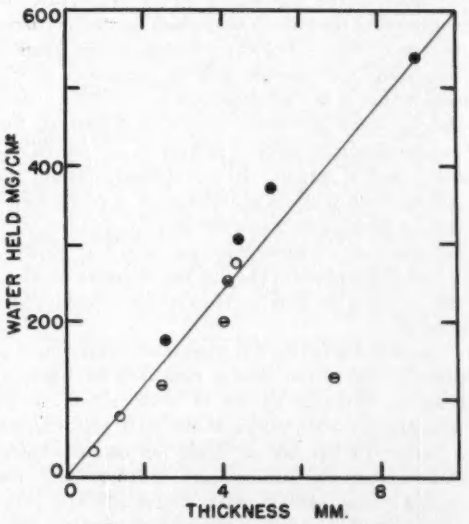

FIG. 6. *Relation between maximum water-holding capacity and thickness, as measured at 7 g./cm.^{2} pressure, for wool fabrics. Felts are indicated by filled-in circles; woven or knit fabrics by open circles; and napped fabrics by circles with horizontal bars.*

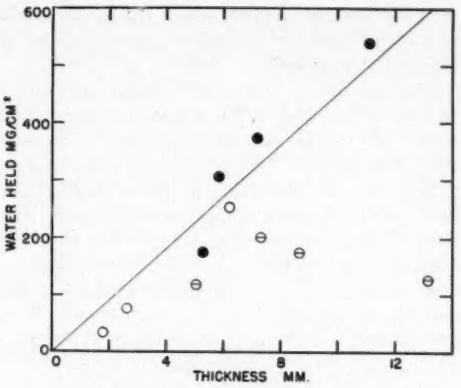

FIG. 7. *Relation between maximum water-holding capacity and thickness, as measured at 0.026 g./cm.² pressure, for wool fabrics. Felts are indicated by filled-in circles; woven or knit fabrics by open circles; and napped fabrics by circles with horizontal bars.*

falling-off in drying rate as compared with thinner fabrics. Figures 6 and 7 indicate that the water in these fabrics is held in the interior, with a fringe of fibers in the nap which serves to increase the thickness of the still air film which forms the barrier to flow of heat. The effectiveness of this fringe in insulating the interior will be decreased to the extent that it is itself kept wet by capillarity, and, judging from the rates shown in Figure 4, this compensation is rather effective in all except the most highly napped fabric studied. Thus, the general lack of effect of differences of fabric structure on drying rate arises not only from the smoothing effect of air films but also from the capillary action of the fibers in keeping the moisture distribution uniform as long as there is any liquid water present.

The relation between thickness and water-holding capacity for cotton fabrics indicated by Figure 5 is 0.45 g. water per sq. cm. of fabric per cm. thickness, and for wool fabrics at the same pressure, 0.6 g. water per sq. cm. of fabric per cm. thickness. However, at the low pressure, 0.026 g./cm.², the compact wool fabrics show practically the same relation as the cotton at the higher pressure. For the extremely nonhygroscopic synthetic fiber Vinyon, the water-holding capacity per unit thickness is approximately half that for cotton. Nylon is intermediate in amount of equilibrium water content and, on the basis of limited evidence, appears to be intermediate in liquid water-holding capacity. However, nylon fabrics are almost always thinner than cotton fabrics in similar service uses, and this, together with the smaller amount of adsorbed moisture between equilibrium at saturation and at the drying conditions, contributes to the shorter drying time.

All the results in the present paper refer to free exposure on a line, in which relatively thick layers of immobilized air determine the rate at which heat can flow into the wet fabric. Under other conditions, such as industrial drying on heated cans, or for clothing worn on the body, the rate of drying can be expected to be influenced by fabric structure and by the amount of contact with the source of heat. This can vary appreciably for the different fibers and for different structures, as has been shown in studies of the sensation of chill and of steady state temperature [2].

Summary

The following results have been obtained for fabrics that are freely exposed to air of low velocity, corresponding to household drying on a line.

1. The major portion of the time required for drying is occupied by the removal of liquid water, which takes place at a constant rate for any given fabric.

2. Drying rates calculated as percent of fabric weight vary with fabric weight, but when expressed as weight of water per unit area of surface are nearly uniform for fabrics up to 10 mm. thick.

3. The rate-governing factor is the thickness of the films of relatively still air near the fabric surface, which under the conditions of these trials is equivalent to 2.4 mm. of still air. This layer smooths-out the effects of surface irregularities.

4. The only large difference in drying rate in these studies arose from a very high and open nap, in which the free-standing hairs appear to have an effect in increasing the thickness of the insulating layer, which is not compensated for by their being wet by capillarity.

Acknowledgment

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New Automatic Cotton Colorimeter for Use in Cotton Quality Specification*

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MEASUREMENTS of cotton color made in the laboratories of the United States Department of Agriculture for more than 20 years have provided a fund of background information on color of cotton, of the grade standards, and of cottons differing from those used in the grade standards which has been useful in the laboratory. Now, however, a new automatic cotton colorimeter has been developed which is intended to serve as an aid in the classing room.

Many applications of this new instrument to cotton color still need to be studied. However, on the basis of information obtained by using previous methods, certain applications can be made immediately. The present report describes these applications, and warns of interpretations that cannot be made correctly without a knowledge of the various factors that make up the grade of cotton.

For cottons that are within the range of the samples in the grade standards and are similar to them in combinations of color of lint, in color and quantity of foreign matter, and in ginning preparation, the colorimeter becomes essentially a "grader." But for samples that are not like the standards in the relationship of these three grade factors—being perhaps more spotted; or being combined with more leaf and better color; or having poor color and a small leaf content, as, for example, in the gray cottons; or perhaps having the same amount of leaf but being unusual in color, as, for example, being very light in color; or possibly being grassy—the color indicated by the instrument must be interpreted on the basis of a suitable weighting of the separate factors involved. The man who knows cotton is able to make such interpretations, and thus can make use of the instrument as an aid in cotton grading; the man who does not know cotton should strictly limit his interpretation to that of the average color of the sample. In the one case the instrument can become an "assistant grader"; in the other case it should remain a "colorimeter."

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Description of Nickerson-Hunter Cotton Colorimeter

The new instrument is based on a satisfactory application of the Hunter Color and Color-Difference Meter to problems of raw cotton measurement. It was found, as shown in Figure 1, that for the limited range of cotton colors a plot of Hunter's coordinates, R_d and b, provided, without conversion, a chart which is reasonably similar to that of long-established cotton measurements which are plotted in terms of Munsell value and chroma.

Since the Color-Difference Meter worked so well, specifications were written for a completely automatic instrument, which was to embody the photocell and filter combinations of the new instrument. The requirements were that the instrument maintain itself in standardization, be direct-reading on a two-dimensional scale, measure automatically, and show values graphically and simultaneously for reflectance and yellowness in a range of 40%–90% R_d and 0–20 units of $+ b$.

Such an instrument was delivered for use in January, 1950. Since then it has been in almost constant operation, having already measured many thousands of cotton samples in preparation for the Universal Cotton Standards Conference which was held in Washington in May, 1950.

The operator places a sample of cotton over the sample window and steps on a foot switch. Two indicators under the chart diagram move automatically to a position of balance. Since a chart of the color of the grade standards appears on the glass panel, the operator can check a test sample against a particular position within each grade and then pass or reject it on the basis of a comparison of results with the position of the standard indicated on the instrument chart.

A top view of this new, automatic, self-standardizing instrument is shown in Figure 2; the interior of the instrument is shown in Figure 3. In Figure 2 a cotton sample is shown in position over the exposure window of the instrument, the operator has just stepped on the foot switch, and the

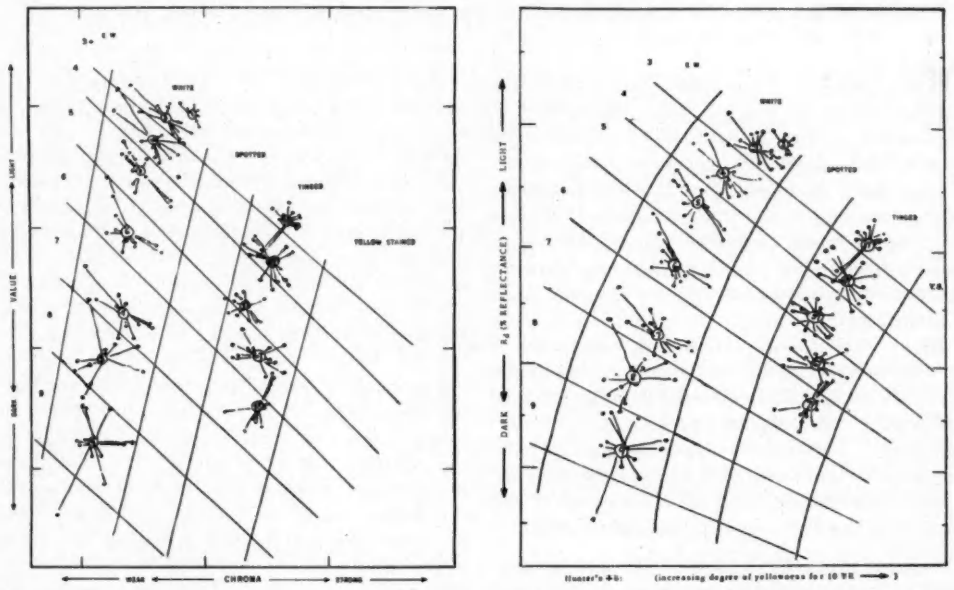

FIG. 1. *Color measurements recorded in the diagram at the left were made in 1946 by disc colorimetry and were plotted for Munsell value and chroma. The same information is shown in terms of Hunter's* R_d *and* +b *color factors in the diagram to the right. For each grade the average color of each of 12 samples in each grade standards box is indicated in relation to the average for that grade.*

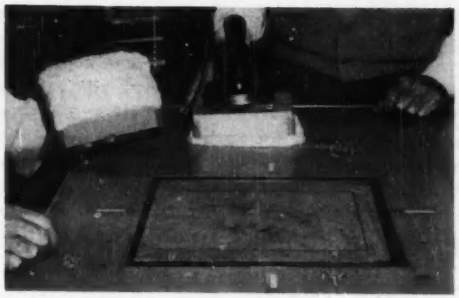

FIG. 2. *Top view of Nickerson-Hunter Cotton Colorimeter, showing a cotton sample in place over the viewing window of the instrument. The result is shown by indicators that move under the translucent center panel, on which color positions of the cotton grade standards are indicated.*

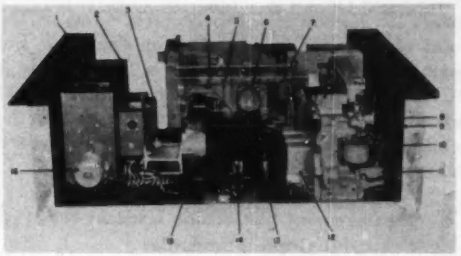

FIG. 3. *Interior view of instrument from the front. Numbers identify components.* (1—*Sample area.* 2—*Exposure head.* 3—*Lamp guard.* 4—R_d *indicator.* 5—*b indicator.* 6—R_d *balancing motor.* 7—R_d *slide wire.* 8—*Amplifier off-on switch.* 9—*Lamps-off switch.* 10—*b slide wire.* 11—*b amplifier.* 12—*Relays.* 13—CV *transformer.* 14—*Lamp for indicating scale.* 15—*Comparison balancing motor.* 16—*b balancing motor.*)

indicators have moved to a position of balance directly under the cotton scale diagram which appears on the translucent glass panel in the center of the instrument. One of the indicators moves in a vertical direction to indicate change in reflectance of the samples, R_d; the other indicator moves in a horizontal direction to indicate change in degree of yellowness of the cotton, $+ b$.

The cotton grade diagram used on the instrument is based on measurements of standards that were passed at the 1946 International Grade Standards Conference and that have been in effect since August 1, 1947.

A numerical code for use in identifying the grade number and color classification of equivalent grades of American Upland cottons is given in Table I. Use of the same code by all who use the new instrument is desirable. A zero added to the code for spotted and gray cottons is suggested to identify "light spotted" (classed as 30) and "light gray" (classed as 60). The first number in a code designation is the grade number, except when the two-digit number 10 is used in the first position to indicate "Below Grade." The second number indicates the color class designations—these range from 1 for Extra White through 5 for Yellow Stained as the yellowness increases, and 6 for Grays. The code 5–1 is interpreted as Middling Extra White.

If more precise information is needed than that supplied by the use of a code referring to official grade standards, then a code consisting of measure-

TABLE I. CODE DESCRIPTION FOR GRADE OF AMERICAN UPLAND COTTON

Grade name and number			Grade color class					
			Gray (G)	Extra White (EW)	White (Wh)†	Spotted (Sp)	Tinged (T)	Yellow Stained (YS)
Name	Symbol	No.	6	1	(2)†	3	4	5
Middling Fair	MF	1			1*			
Strict Good Middling	SGM	2			2			
Good Middling	GM	3	36*	31*	3	33*	34	35*
Strict Middling	SM	4	46*	41*	4	43*	44	45*
Middling	M	5	56*	51*	5	53*	54	55*
Strict Low Middling	SLM	6	66*	61*	6	63*	64	
Low Middling	LM	7		71*	7	73*	74	
Strict Good Ordinary	SGO	8		81*	8			
Good Ordinary	GO	9		91*	9			
Below Grade	BG	10						

* Grades for which standards are descriptive.

† For the white grades, use of the color class symbol or code number is not necessary if the meaning is clear without them.

ments for R_d and $+b$ can be used, either in the form of a decimal or a common fraction. For example, for $R_d = 71$, and $+b = 10$, the code is 71.10 (or 71/10). The reflectance number should precede the yellowness number in order to keep the results in the same order as for the Munsell value/chroma specifications.

Measurement of Cottons Used in the Grade Standards

As is well known, grade of cotton depends upon color of fiber, amount and kind of foreign matter, and roughness or smoothness of ginning preparation. As is also known, the U. S. Standards for grade of American Upland cotton, known as Universal Standards, consist of 33 grades, 13 of which are represented in physical form.

Early in the color-measurement work on cotton, correlations were made of hue, value, and chroma measurements of the white cotton standards against their grade numbers. These correlations were as high as 98%, the value and chroma factors contributing about equally to the correlation, but hue not at all. On the basis of these correlations, diagrams for plotting the color of cotton since that time have been two-dimensional.

Color measurements of cotton samples are made on the basis of the composite appearance of the sample—in other words, the color measurement represents an average of the contribution made to the color of a sample by the color of fiber, the amount, color, and kind of foreign matter, and the roughness or smoothness of its ginning preparation.

Since the combination of color of lint and of foreign matter in cottons used in the grade standards fits a pattern of what is normal for each grade, it could be expected that a correlation of the amount of foreign matter against grade would be about as high as the correlation found for color measurements. In other words, for cottons already carefully selected for use in the standards, measurements of either the color or the amount of foreign matter in a sample would allow an accurate prediction of its grade in all except a very few cases.*

* Regarding foreign matter in cottons that are used for the grade standards, reference may be made to an article by the author in TEXTILE RESEARCH JOURNAL, April, 1950, pages 277–8, in which detailed measurements are given for foreign-matter content in bales used in the 1936 and 1946 standards.

Because the grade standards are put up in a specific manner out of cottons already selected by eye as a good match in color, leaf, and preparation for each position in the grade boxes, and because they are put up in cartons holding about the same amount of cotton for each sample, it has been possible to make immediate application of the new instrument to the grade-standards work. The grade diagram, based on measurements of cottons so selected and measured, applies to other cottons similarly selected and similarly prepared for measurement.

In Figure 4 the results for several typical positions in the standards boxes are shown. The large open circle in each grade block represents the average for the grade in 1946. The arrow from that circle points to the position of the color to be matched. Dots represent samples accepted as being within a reasonable tolerance for the position; crosses represent samples considered to be too far off to be acceptable. Although it is known that even for uniform bales there are differences between samples from the same bale, this is the first extensive set of data demonstrating the degree of color variation that exists between samples from such bales.

Measurement of Commercially Available Cottons

Tolerance is not the only factor that must be considered. It has been possible to make immediate use of the new instrument for such a selected series of cottons as those prepared for the grade standards because these cottons are carefully selected to represent a normal combination of color, leaf, and preparation for the grade each represents. The amount of cotton put into each carton is about the same, and the samples are measured in the cartons, a given pressure being applied at the time of measurement.

For such samples, the colorimeter becomes almost a "grader." Note the *almost*. For it should be kept in mind that this instrument is intended as an aid to the classer; it cannot replace him. And the reason that it cannot is that the instrument sees only one thing. It sees the average color of whatever appears on the face of the sample placed over its sample window. If the conditions under which a sample is tested are not the same each time, the measurements should not be compared.

Aside from the question of a standardized method of making sample measurements, there are other

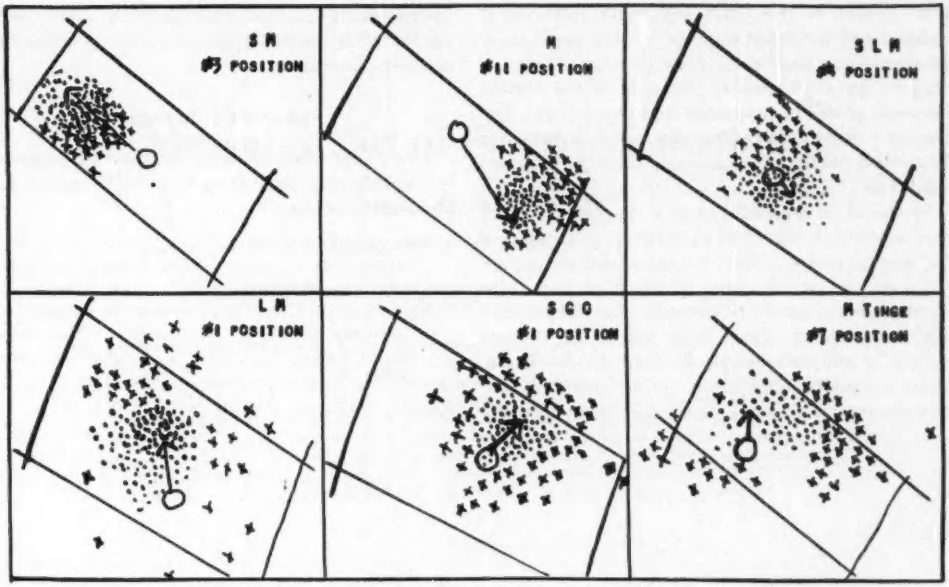

FIG. 4. *Color measurements of many samples from bales selected to be a close match for 6 typical positions in the grade standards. Note that the amount of scatter increases for the lower grades.*

matters that must be taken into consideration before one should attempt to judge the grade of cotton on the basis of color measurements. No colorimeter yet designed can tell whether the color it reads is the result of spots, of amount or color of foreign matter, or of general background color; all kinds of combinations can be used to produce the same average color. A classer, however, would immediately know the correct color classification. For example, a classer can see a given amount of leaf in a sample, whether it be light or dark in color. He can differentiate the general class of Gray cottons from White or Extra White cottons. Once he identifies a sample as Gray and not White, the instrument can then help him to classify it into the correct grade of Gray if a diagram for Gray standards is prepared for his use.

The same thing is true of Spotted cottons. There may be so little spot in some samples that the instrument measurement will show the same average color as for a White grade. Yet the classer would see the light spot, and by using the instrument could soon learn to place it always in the same grade. Enough tests must be made in the laboratory on cottons of all kinds in order to make up suitable diagrams. By using an automatic instrument it should be possible to maintain more constant interpretations of applicable grades for samples not represented in the grade boxes. In fact, intelligent use of this instrument should enable many more classers in the future to obtain results as accurate as those obtained by the very few who in the past have been expert in assessing color differences in cotton.

If mechanical harvesting comes into more general use, or if more effective methods of cleaning cotton at the gin are developed, the relations of color, leaf, and preparation officially set up for the present grade standards might no longer hold for large portions of the crop. Should this occur it would be necessary to study such samples in sufficient quantities, both to provide adequate data for the development of suitable diagrams for aiding the classer to determine consistent grades as they are related to the grade standards and to make it possible to recommend suitable changes for future standards.

From studies of cleaning methods, something is

now known of the color and trash relations in cleaned and uncleaned samples. A few preliminary measurements have been made on cleaned lint and on grey fabrics in order to follow-up on the relation between grades of raw stock and cleaned lint, and the color of grey cloth made from it; this study can be applied further to measurements on the bleached materials.

It should be remembered that the color range of the instrument described in this report is selected for that of cotton only. If other color ranges are required, or use of three in place of two color dimensions (as would be necessary for differentiating "pink whites" from "blue whites" or "yellow whites"), adaptations would need to be made. However, such adaptations can be made by the manufacturers, since the principles upon which the instrument is designed are completely adaptable to use for other limited ranges of colors, in either two or three dimensions.

Literature Sources

This paper summarizes information that appears in the following papers, each of which carries full literature citations:

1. Nickerson, D., Hunter, R. S., and Powell, M. G., New Automatic Colorimeter for Cotton, *J. Optical Soc. Am.* **40**, 446–9 (1950).
2. Nickerson, D., Color Measurements of Cotton, Preliminary Report on Application of New Automatic Cotton Colorimeter, U. S. Dept. Agr., Apr. 1950, 18 pp., illustrated. (Processed.)

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Measurement of Fiber Orientation

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Abstract

A method is described for estimating the extent of fiber orientation in lap, sliver, etc., thus making possible a quantitative evaluation of the effectiveness of carding and drawing operations in aligning the fibers. In principle, the method involves clamping the sample in a special device, cutting out a section of fixed length (*e.g.*, ½ in.), and straightening out the fibers by combing. Then, all fibers found to be longer than ½ in. must have been out of alignment in some way in the original section. From the ratio of the portion in excess of ½ in. to ½-in. portion an orientation index is calculated. This index serves to arrange the samples in the following expected order of increasing orientation: card sliver, drawing sliver, finisher drawing sliver, and roving. Combed roving shows almost complete parallelism. Applications of the method are suggested.

Introduction

Textile operations such as carding and drawing are designed in part to increase the parallelism of fibers. Measurement of fiber orientation at various stages in processing would be very useful in evaluating the effectiveness of these operations. The following considerations suggest a method for estimating such orientation.

If a section of some fixed length (*e.g.*, ½ in.) is cut out of a length of sliver or roving, and the fibers in the section are straightened and sorted out according to length, then all fibers found to be over ½ in. long (from a ½-in. section) must have been out of line in the sample—bent or twisted or straight but at an angle to the sliver axis (see Figure 1). It is recognized that not all of the nonparallel fibers are found by this procedure, because in some cases fibers lie only partly within the cut section, and short fibers less than ½ in. long will not be counted, regardless of their orientation. Nevertheless, any fiber longer than ½ in. must have been out of line somehow. It appears, therefore, that some indication of the extent of departure from orientation can be obtained by this procedure.

In the use of such a method, two problems arise—one in technique, the other in interpretation. As to technique, an effective and reasonably rapid method is needed for straightening the fibers and sorting the long from the short ones; means for doing this are described in the next section. But after the fibers have been sorted, how are the results to be interpreted in terms of orientation? Preferably, orientation should be expressed by a single number, but to do this is difficult because of the difficulty in defining orientation, or a departure from it, in precise terms. For instance, which should be regarded as exhibiting greater departure from parallelism: a few fibers markedly out of line or many fibers slightly out of line? Should a fiber which is bent double with both halves parallel to the axis of the sample be counted as out of line or not? While the meaning of parallelism of fibers is quite clear, departure from parallelism or disorientation may be of several kinds and hence cannot be unambiguously expressed by a single number. It has been found possible, however, by the method here described to assign an index number which is consistent with experience and expectation. In the absence of an alternative method of measuring orientation, a check on the

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validity of this index is lacking. This very lack emphasizes the need for some kind of measure.*

Methods

The first method used for estimating orientation was to clamp the sample (sliver, roving, etc.) between two brass plates, the upper one having parallel edges ½ in. apart. The sample was trimmed off with a razor blade along the two parallel edges, leaving the ½-in. section underneath. The fibers in this section were then sorted according to length by means of the Suter-Webb Sorter, and the ratio of the weight of fibers longer than ½ in. to the total weight of the section was taken as a measure of orientation. The principal objection to this method was the length of time required to sort the fibers according to length (more than an hour).

With perhaps some loss in directness of measurement but at a very considerable gain in convenience, the following modification was adopted. The cutting device used consists of four parts, shown disassembled in Figure 2 and assembled in Figure 3. Two base blocks are grooved to fit snugly together; these are provided with pivoted screws for clamping in place two brass plates, one of which (the cutting plate) is machined to a known width (*e.g.*, ½ in.) and the other of which serves to clamp one end of the sample during the combing operation. Both plates have holes to fit over pins in the base blocks, which serve to line them up properly and to bring them back to the same initial position once they have been removed. The lower side of the clamping plate is recessed slightly to within about ⅛ in. of each edge in order to provide a better hold on the sample. Interchangeable cutting plates of several widths are provided in order to permit study of the effect of variation in the length of the section cut.

Procedure

The procedure employed may best be followed by studying Figures 2–6. A cardboard square, against which the cut is to be made, is laid on the assembled base blocks; a length (or several lengths) of the sample to be studied is laid on the cardboard,

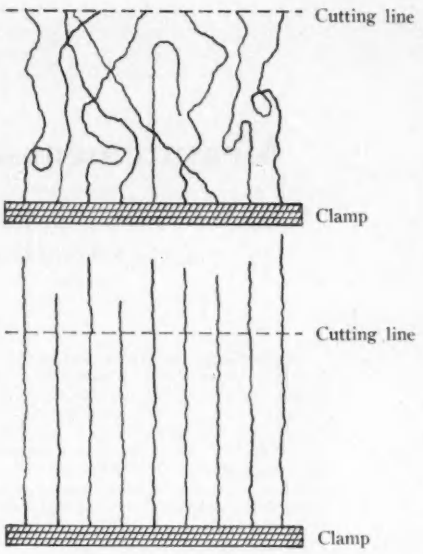

FIG. 1. *Schematic representation of fibers before combing* (top) *and after combing* (bottom).

its axis perpendicular to the adjacent faces of the blocks; and the two plates are then clamped in position, leaving the ends of the sample exposed. With a razor blade, the sample is trimmed off closely against the outer (right) face of the cutting plate, the trimmed-off portion being discarded (Figure 3). The cutting plate and corresponding base block are then removed, the cardboard is bent down sharply to expose the tuft of fibers, and the tuft is combed out with a small comb having about 16 steel teeth per in. (Figure 4). Combing should be gentle, gradually working from both top and bottom of the tuft into the center, so as not to break fibers. The object is to straighten the fibers as completely as possible; in so doing, all fibers in the tuft which are not held by the clamping plate are removed. After combing, it is usually necessary to pull out a few loose fibers near the end of the tuft with the fingers. The combed-out portion (*C*) is collected and weighed on a torsion balance.

After the base block and cutting plate have been replaced, a fringe of fibers is left extending beyond the cutting plate (Figure 5). These are cut off, collected, and weighed (extended portion is designated *E*). The clamping plate is then removed and

* Morton and Summers of the University of Manchester have reported a tracer-fiber technique for investigating fiber arrangement (*J. Text. Inst.* **40**, 106 (1949)) and have applied it to a study of fiber rearrangement during drafting (*ibid.* **41**, T349 (1950)). This technique involves the direct observation of the orientation of certain dyed fibers, present in known proportion among the unmarked fibers.

the excess of the sample to the left of the cutting plate is cut off and discarded. Finally, the cutting plate is again removed (Figure 6) and the "normal" portion (N) of the sample is weighed. The weights of these three portions—C, E, and N—are the quantities that are used in estimating the extent of orientation in the sample.

Significance of the Weights C, E, and N

Before any interpretation of results in terms of fiber orientation is possible, the significance of the three portions must be considered. With regard to C, it is clear that if the sample consists of continuous filaments, $C = 0$. If the material contains fibers which are all of the same length, the ratio of the portion combed out to that held by the clamping block—*i.e.*, $C/(E + N)$—called the *combing ratio*, depends upon the fiber length L and the length of the section cut, S (the width of the cutting plate). Assume for the moment that all fibers (length L) are parallel and that the sample is uniform, with the same number of fibers in all cross sections. Then, for $S = L$, it is readily seen that half of the fibers in the section will be combed out, and hence the combing ratio is 1. For S less than L, the ratio is less than 1; when S is very small, C and $C/(E + N)$ approach zero.

For materials such as cotton sliver, in which there is wide variation in length of fibers, the situation is much more complex than for materials like staple rayon, in which the variation is small. Nevertheless, in a general way, the above considerations may be assumed to hold for each fiber length. The amount combed out is proportionately smaller as the width of the cutting plate is made smaller. There is, naturally, a limit below which it is impractical to reduce the width, S. In the first place, other things being equal, the fringe of extended fibers (portion E) becomes smaller as S is reduced. Since, for most samples studied, E weighs only a few milligrams, or tenths of milligrams, this portion becomes too small to measure accurately if S is much smaller than $\frac{1}{2}$ in. In the second place, the smaller S is the greater the probability that a bent or hooked fiber will be cut so as to appear as two parallel fibers, resulting in a decrease in significance of the measurement. For these reasons, $\frac{1}{2}$ in. has been chosen as the minimum width, but for short-staple cotton it might be necessary to use smaller cutting plates in spite of the objections.

The quantity E is the weight of fiber protruding beyond the cutting plate after combing and straightening the sample. As was pointed out above, all these long ends must have been curled or bent under the cutting plate before combing. These long fibers could be withdrawn from the tuft left after combing, and their weight compared to that of the residual fibers to give a measure of departure from parallelism, as was done in the sorting technique, but in addition to introducing another step, this procedure may give results that are misleading. Consider, for example, a sample of filament rayon with 25% of the filaments, due to twist or other causes, arranged at an angle of 10° to the axis of the sample. If a $\frac{1}{4}$-in. section is cut and combed out as described, 25% of the fibers in the tuft will be 0.508 in. long (0.500 × sec 10°) and the other 75% 0.500 in. long. If the first group is withdrawn and the two groups weighed, the ratio of weights will be 0.34. But if the extended portion (0.008 in.) is cut off and compared with the residue, as recommended in the proposed procedure, the ratio E/N will be 0.004. If similar calculations are made for another sample in which 25% of the filaments are out of line by 20°, the corresponding ratios are 0.35 and 0.016, respectively. The first figure in each case—0.34 and 0.35—is an approximate measure of the *number* of fibers out of line, without regard for the extent of disorientation, and hence is nearly the same for the two samples. The second figure—0.004 or 0.016—is a much better indication of lack of orientation. Actually, instead of the ratio E/N, the related quantity $(1 - E/N) \times 100$, called *orientation index*, is used to express degree of orientation. A sample in which the fibers are all parallel ($E = 0$) will therefore have the orientation index 100, while samples with nonparallel fibers will have lower indexes. (Again, it should be noted that for most practical cases the situation is much more complex than for the examples discussed above. Nevertheless, the general conclusions drawn from examination of the simpler cases are still valid.)

For convenience, the symbols and definitions of terms introduced are summarized:

Combed-out portion	C
Extended portion: long ends extending beyond cutting plate after combing	E

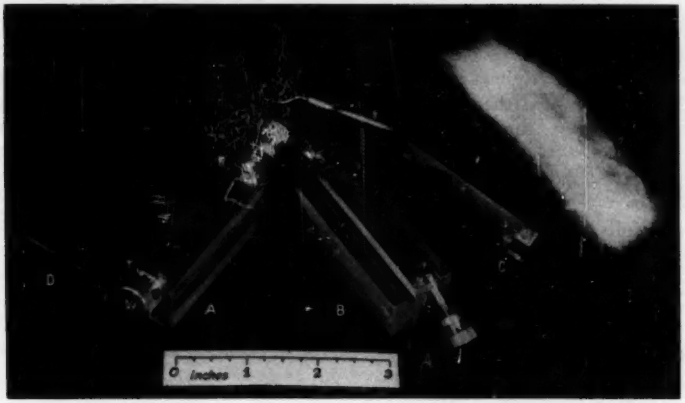

FIG. 2. *Device for measuring fiber orientation; parts are separated:* A, B, *base blocks;* C, *cutting plate;* D, *clamping plate. Comb, cardboard square, blade, and sample are also shown.*

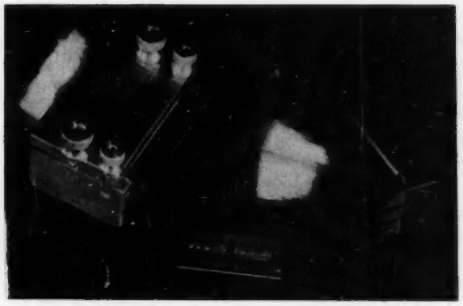

FIG. 3. *Device is assembled. Excess sample has been trimmed off along outer (right) face of cutting plate.*

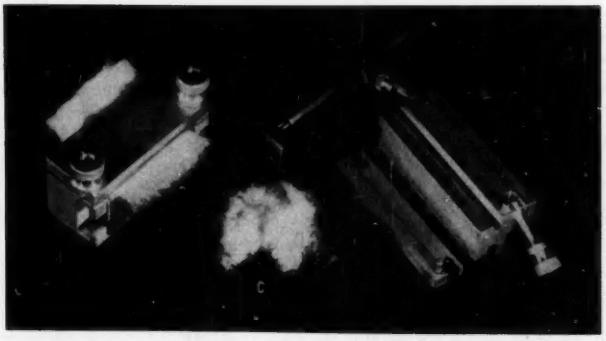

FIG. 4. *Sample is combed. Cutting plate and corresponding base block have been removed; cardboard has been bent down; and the fibers have been combed out. The combed-out portion* (C) *is shown in the center.*

FIG. 5. *Extended fibers are shown. Cutting plate and block have been replaced, preparatory to cutting off the long fibers.*

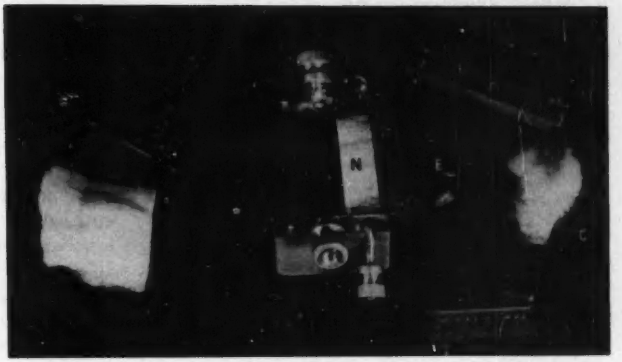

FIG. 6. *Test is completed. Extended fibers* (E) *have been cut off, the clamping block has been removed, and the excess sample at the left of the cutting plate has been trimmed off. The normal portion* (N) *is left under the cutting plate (shown removed). The three portions are ready for weighing.*

Normal portion: fibers left under cutting plate after combing	N
Combing ratio	$C/(E + N)$
Orientation index	$(1 - E/N) \times 100$.

Experimental Results

After some preliminary tests, the first factors to be studied systematically were (1) reproducibility of results and (2) effect of varying the width of the cutting plate. Both factors are illustrated by the data given in Table I. Cotton sliver ($1\frac{1}{16}$-in. staple) was used and 18 successive sections were cut out, using in rotation three cutting plates $\frac{1}{2}$, $\frac{5}{8}$, and $\frac{3}{4}$ in. wide. The uniformity of the sliver, as indicated by the approximate constancy in weight of sections of each length, is satisfactory in view of the smallness of the samples. There is no obvious explanation of why the $\frac{3}{4}$-in. sections appear so much more nearly uniform than the shorter sections. The variation in combing ratio, on the other hand, seems high in comparison with the other figures. In accordance with the conclusion arrived at from general considerations above, the combing ratio increases with increasing width of cutting plate. There is no apparent reason for the increase in orientation index as section length is increased; perhaps it is associated with the increase in combing ratio. In spite of the uncertainties, the method does yield approximately reproducible values, and it appears that $\frac{1}{2}$-in. sections may show greater differences in orientation index than do longer sections.

Table II shows the results obtained when the method is applied to different types of materials. Since no other method for determining orientation is available, the accuracy of the results cannot be judged. However, the method does arrange materials in the expected order: combed roving was almost completely parallel; carded roving was somewhat less nearly parallel; drawing sliver was still less; and card sliver was the least nearly parallel. These samples were picked at random, with no known relationship existing among them.

TABLE I. REPRODUCIBILITY OF RESULTS AND EFFECT OF SECTION LENGTH ($1\frac{1}{16}$-IN. COTTON SLIVER)

½-in. section			¾-in. section			¾-in. section		
Wt. of section (mg.)	Combing ratio	Orientation index	Wt. of section (mg.)	Combing ratio	Orientation index	Wt. of section (mg.)	Combing ratio	Orientation index
51.9	0.74	94.8	62.6	0.92	96.0	78.9	1.31	98.6
51.4	0.71	95.8	66.4	1.04	96.7	83.0	1.32	97.9
58.3	0.81	97.8	68.3	1.23	98.8	80.9	1.43	99.0
56.2	0.88	97.3	61.4	1.16	98.6	85.3	1.42	98.9
64.0	0.93	97.3	71.7	1.17	98.3	86.6	1.62	99.0
54.2	0.74	98.2	75.5	0.97	97.4	80.0	1.28	98.3
				Average values				
56.0	0.80	96.9	67.7	1.08	97.6	82.5	1.40	98.6
				Average deviations				
6%	9%	1.0%	6%	9%	0.9%	3%	6%	0.4%
				Maximum deviation				
14%	16%	2%	12%	15%	2%	5%	16%	0.7%

Thus, it should not be assumed that the drawing sliver was prepared from either of the card slivers; hence, it should not be concluded that drawing has relatively little effect in increasing parallelism, as the data might seem to indicate.

In Table III, results obtained with a series of samples taken after each of several operations are given—a single sample of cotton was carried through carding, drawing, and roving. Each value is the average of at least three measurements. In this case, considerable improvement in orientation was found when the card sliver was drawn; further improvement, slight but significant, was observed after a second drawing. Drawing three times made no appreciable change in orientation. It may be pointed out that after the first drawing this particular sample was highly oriented, so that very little additional improvement could be obtained with further drawing. Drawing sliver with as low an index as the sample reported in Table II would probably show a considerable increase in orientation upon further drawing.

Possible Significance of the Combing Ratio

It was shown previously that the combing ratio—*i.e.*, ratio of the weight of fibers combed out to the weight of fibers in the section held by the clamping plate, $C/(E + N)$—is dependent upon the length of the section cut for a given length (or length distribution) of fibers. This conclusion was confirmed experimentally, as shown in Table I, the combing ratio increasing with increasing width of cutting plate. Other factors, however, are also involved, among them the degree of orientation. In the previous discussion, for the sake of simplicity, it was assumed that the fibers were parallel, or nearly so. Because of the regular distribution of fiber ends along the sample, some fibers will be combed out. It may be assumed that the two portions—the one combed out and the one held

TABLE II. MEASUREMENT OF ORIENTATION IN SEVERAL MATERIALS (½-IN. SECTIONS)

Type of material	Combing ratio	Orientation index	Average
Card sliver, I	0.99	87.7	
	1.00	88.1	
	0.98	87.8	87.9
Card sliver, II	1.08	87.1	
	0.94	86.0	
	0.87	88.4	
	1.06	87.1	87.1
Drawing sliver	1.22	89.9	
	1.07	88.9	
	1.28	90.6	
	1.01	89.5	89.7
Roving	0.66	95.3	
	0.69	97.9	
	0.58	94.9	
	0.81	98.3	96.6
Combed roving	0.22	99.1	
	0.27	99.1	
	0.27	99.2	99.1

TABLE III. MEASUREMENT OF ORIENTATION, SHOWING IMPROVEMENT THROUGH DRAWING (§-IN. SECTIONS)

Form	Weight (grains/yd.)	Combing ratio	Orientation index
Card sliver	60	1.55	86.9
First drawing	55	0.78	96.3
Second drawing	53	0.72	97.8
Third drawing	40	0.67	97.6
Roving	—	0.65	98.1

TABLE IV. COMBING RATIO AS AN INDEX OF RANDOMNESS IN FIBER ORIENTATION

Sample	Combing ratio	
	Sample taken in the normal direction	Sample taken 90° to the normal
Bale cotton	3.2	3.5
Picker lap	2.1	3.4
Card strip	2.1	49
Card web	1.8	—

under the cutting plate—are essentially similar and hence that the results obtained for the portion retained are representative of the whole sample. But if a considerable fraction of the fibers is greatly out of line, these assumptions are not even approximately valid. As an extreme case, suppose that, before combing, 80% of the fibers in the cut section are parallel, but that the remaining 20% are at right angles to the others. If it is assumed further that all of the parallel fibers extend clear across the section, then, on combing, none of the parallel fibers will be removed and all of the cross fibers will be. The combing ratio will therefore be $20/80 = 0.25$, and the orientation index 100, since E is equal to zero. The index indicates complete parallelism, even though 20% of the fibers were completely out of line. The difficulty lies in the fact that *all* such cross fibers and none of the parallel ones were combed out, so that the remaining portion was no longer typical of the original sample.

Although the example just considered is extreme, the same difficulty may be met, in varying degrees, in any sample in which there is an appreciable proportion of cross fibers. Samples of card web and picker lap, and even cotton from the bale, were tested, and in all cases high values for the combing ratio were obtained (Table IV). In such cases, it is clear that the orientation index has little or no significance. On the other hand, high values of the combing ratio are indicative of considerable randomness in orientation. Furthermore, if with such materials one cuts and combs two sections taken at right angles to each other, the more randomly the fibers are oriented the more nearly equal will be the combing ratios. In Table IV are shown such comparisons. The normal direction is the direction of delivery of the sample (lap, strip, or web); it is, of course, meaningless when applied to bale cotton. Obviously, bale cotton is randomly oriented. In picker lap there is some alignment, even though the high value of 2.1 for the normal direction indicates great departure from parallelism. In card strip, the same value of 2.1 indicates great disorientation, as visual inspection clearly shows; but when a section is cut in a direction perpendicular to the direction of delivery, 98% of the sample is combed out. Thus, card strip, while highly disoriented, has a strongly preferred direction. A marked increase in orientation is evidenced when card web is formed into sliver.

The combing ratio, therefore, may be used as a rough index of the randomness of fiber orientation. Since no additional work is required for calculating this ratio except weighing the combed-out portion on the balance, it is always recorded. Except when very short fibers are being measured, the ratio should not be much greater than 1, unless there is a significant proportion of so-called cross fibers. When the combing ratio is greater than about 1.5, the orientation index should be regarded as having dubious significance, but the combing ratio itself may be used as an index of relative arrangement of the fibers. The orientation test as described here is best suited to materials such as sliver and roving, in which there is a dominant direction and the fibers are at least reasonably well lined-up.

Several applications of this method for estimating orientation are: determining the effect of card speed and settings on fiber orientation; the effect of repeated carding and the change in orientation with change in speed, separation, and composition of the drawing rolls; further study of the effect of repeated drawing; and possibly a comparison of the effectiveness of different types of drawing frames. The method may also be extended to study fiber arrangement in yarns.

Summary

A simple, rapid experimental method is described for obtaining a measure of the orientation of fibers in various materials—particularly in sliver and roving. The measured orientation index, herein defined, places materials in the same order of relative degree of orientation as experience and observation suggest, but assigns a numerical value to each sample and distinguishes differences that cannot otherwise be observed. For materials such as bale cotton and picker lap, another measure—the combing ratio—provides an approximate measure of the randomness of fiber arrangement. With this method as a guide, the operations of carding and drawing may be investigated to observe the effects of various changes on fiber orientation.

Acknowledgment

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Tire-Cord Compression Fatigue*

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I. Introduction

Much of the work that has been presented on tire-cord fatigue has been on what may be more specifically called tension fatigue. Tire-cord fatigue has been studied by such methods as the repeated stretching of a cord between fixed grips [4] and by the longitudinal vibration of a cord-weight combination [3, 6, 10]. These tests are essentially means of gradually breaking down or fatiguing the cord by the frequent repetition of small tensile stresses. Actually, tire-cord fatigue may often involve more than repeated tensile stresses, and, although the tension-fatigue test is a very important one, it does not take enough parameters into consideration in order to give a complete account of what actually occurs in practice.

When an inflated tire—which is under tension throughout—is loaded, part of the tire will become subjected to an increased tension stress and part of it either to a relieved tension stress or to a positive compression stress.

To illustrate this, one may imagine a rubber box which has a cubical shape when it is inflated. When inflated it is under tension throughout; but if a load is applied to the top of the box, some of the tension in the vertical walls will be relieved, and, if the load is great enough, a positive compression will be produced in these vertical walls. Up to this point it has been assumed that the walls are not bowing out under the load but are maintaining a prismatic shape for the box. At the same time that either tension has been relieved or a positive compression has been produced in the vertical sides of the box, there will be an increase in tension in all faces of the box in the horizontal direction. This must occur to compensate for any relieved vertical tension and from any decrease in the volume of the box, pressure × volume being constant. Should any bowing of the sides of the box then be allowed to occur, accompanied by a decrease in the height of the box, longitudinal compressions will still remain and there will be an increase in tension in the lateral direction because of further decrease in the volume of the box.

The part of a tire that rests on the road may be thought of as analogous to the rubber box and subject to compression and increased tension stresses much in the same manner as is the box. In addition, there will be another lateral tension in the contact region which must be considered; this is produced owing to the fact that, irrespective of inflation, the part of the tire resting on the road is more inclined to bulge laterally while the rest of the tire remains restrained. As a result, the unrestrained region must stretch and produce a lateral tension.

Of course, all other parts of the inflated tire will be subject to increased stress (tension) as well as the region near the road. However, the more obvious distortion of the region near the road, particularly when the tire is highly loaded, indicates that this is the part to consider in any analysis of fatigue stresses.

The part of the tire resting on the road will be distorted to a degree which will depend upon the conditions of inflation and loading. Under normal inflation and moderate load there will be little increase in tension in the lateral direction of this distorted region. There will be no positive compression in the longitudinal direction but only some relief of the tension of inflation. However, if inflation is reduced and the loading increased, a point may be reached where there will be considerable tension in the lateral direction and a positive compression in the longitudinal direction. It is this latter situation with which we are concerned in the present discussion of cord fatigue.

The cords of the tire take a spiral path on the tire and they cross each other in alternate plies. Under

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the particular low-inflation, high-load conditions just referred to, any cords in the distorted region which run in the direction of increased tension are themselves subjected to an increased tension. Any cords in the distorted region which run in the direction of compression will be subjected to a longitudinal compression.

As a tire under these particular conditions revolves, all parts of it must pass through the distorted region and all cords must go through conditions of increased tension and longitudinal compression. In other words, the cords will go through a compression-tension cycle and it is this cycle, repeated a great many times, which can cause eventual cord breakdown and sidewall fatigue failure. It is this cause of fatigue with which we are concerned in this discussion, and it is the compression part of the fatigue cycle in which we are mainly interested.

One of the easiest ways to show that longitudinal compression can exist in the region of the tire resting on the road is to peel off part of the rubber sidewall. Figure 1 shows this for a tire under the conditions of low inflation and heavy overload. It can be realized that the sidewall is compressed longitudinally because a buckle resulting from the compression can readily be seen. The point of buckling shown in the figure is not necessarily the point of fatigue failure for this particular tire. The illustration is only intended to emphasize the idea of sidewall compression.

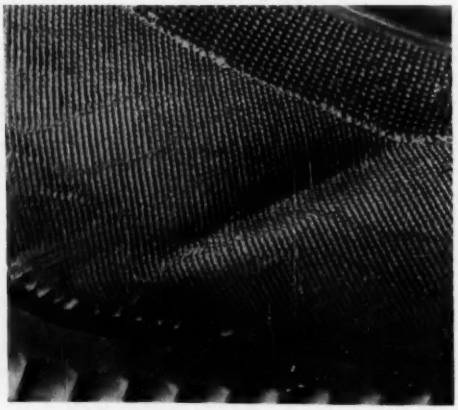

FIG. 1. *Stripped sidewall, showing the effects of longitudinal compression on tire cord.*

To consider the nature of the longitudinal-compression stress and strain in a tire cord, imagine gripping a free cord at points close together and compressing it longitudinally in the same way that one compresses a spiral metal spring. The cord plies spread out as a result of the longitudinal thrust and fold like springs being compressed.

Now imagine the cord encased in rubber, as shown in Figure 2. If a longitudinal stress is applied to this cord by compressing the rubber block longitudinally, it can be imagined that the spiral plies of the cord will still behave like spiral springs, but because of the lateral restraint of the rubber, the spiral plies cannot spread out as before to relieve the thrust. The cord plies must now rub and crush against each other.

Figure 3 shows the longitudinal compression of a cord under lateral restraint. The photographs are of the cord in transparent polyvinyl butyral, which was compounded to have a modulus roughly the same as that of rubber. It is the restraint to the lateral bulging shown in the figure which produces the longitudinal-compression stresses that fatigue the cord.

Imagine further a cord which has no twist at all but is simply a bundle of parallel fibers or filaments. If this cord in the free state is compressed longitudinally, the fibers or filaments can spread out and bend without suffering any damage. But if this cord is encased in rubber and compressed longitudinally, the fibers or filaments can no longer spread out as readily, and they must undergo a certain amount of buckling during the longitudinal compression.

To summarize the idea of longitudinal-compression strains in a tire cord, it may be stated that

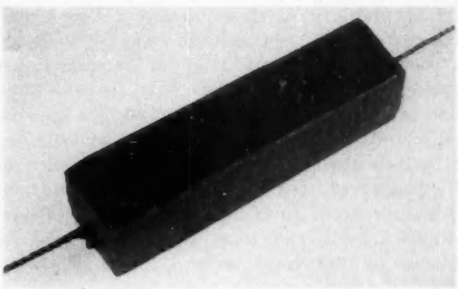

FIG. 2. *Cord encased in block of rubber.*

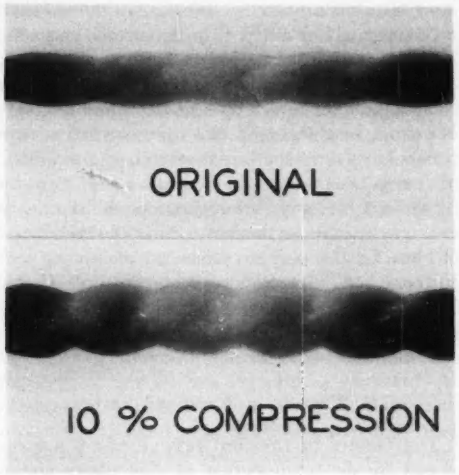

FIG. 3. *Longitudinal compression of a cord (in polyvinyl butyral) under lateral restraint.*

these strains will occur because of the lateral restraint effected by the rubber, and, in addition, because of the packing of other neighbor cords. The strains can be imagined to involve the rubbing and crushing of the cord plies against each other and some component of buckling of the fibers or filaments.

It has been implied that a cord in a tire has a degree of stiffness to compression because of lateral restraint. This stiffness of the individual cords introduces a stiffness factor for the tire sidewall as a whole. This sidewall stiffness factor will determine a particular compression-stress pattern which will determine the particular spot on the cord which is to be most severely affected. In other words, there will be a particular region where fatigue failure will occur.

Under conditions of rapid breakdown of tire sidewalls where heat is not an important factor, we can assume that high loading, underinflation, or both, were the primary causes, and that these conditions produced detrimental, positive longitudinal compressions along the cords to start the breakdown. An aid to the damaging compression stresses are the increased tension stresses, which originate at the same time and as a result of the same conditions.

To summarize, then, the particular fatiguing action discussed here is a compression-tension cycle which is repeated a great many times; and eventually the cord breaks down as a result of the combination of compression and tension stresses.

A cord-rubber fatigue test which takes compression stresses into account is the Goodyear compression-tension fatigue test [1, 9]. In this test, cords are set longitudinally in a rubber tube; the tube is bent through 90° and is then twisted at a fairly high frequency about the bent longitudinal axis. The cords go through a compression-tension cycle by passing through the inside and outside of the bent-tube configuration and are eventually failed as a result of this fatiguing action.

II. A New Compression Fatigue Test

As another approach to the study of the longitudinal-compression stress in a tire cord (combined with a tensile stress) the simple device of compressing and extending little blocks of rubber containing the cord has been chosen. (See Figure 2.) These little blocks are $\frac{1}{2}$ in. $\times$ $\frac{1}{2}$ in. $\times$ 2 in., and the cord runs lengthwise through the center. At each end of the block $\frac{3}{4}$ in. of the cord is reinforced with other fabric, thus leaving a $\frac{1}{2}$-in. length of cord in the middle of the block surrounded only with rubber. In order to aid in the gripping of the samples, the ends are given a single wrap of cotton cord (not shown in Figure 2).

Figure 4 shows a simple machine for producing the desired compression-tension cycle on these blocks. It consists essentially of two rotatable steel discs which are mounted concentrically $\frac{1}{2}$ in. apart. One of these discs is on a swivel so that it can be skewed with respect to the other. The other disc is coupled to a motor.

The rubber blocks are mounted across the rims of the two discs, coupling them together, while the

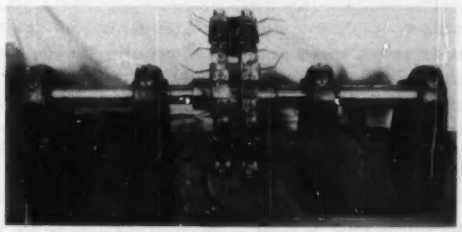

FIG. 4. *Fatigue machine with samples mounted.*

discs are in a parallel or neutral position. The swiveled disc is then turned a given amount and locked in the new position. If the coupled discs are then rotated, the rubber blocks must go through conditions of longitudinal compression and extension, passing, respectively, through the maxima of these conditions at the points where the discs are closest and farthest apart.

Thus, a compression-tension cycle may be produced in the tire cord. A frequency of 1,900 cycles per min. was used for the test. This simple, but highly effective, method of producing reciprocating action by rotation was devised at The B. F. Goodrich Research Laboratory [5] and has been used in other rubber-flexing tests.

So far the test has been run as a constant-deflection test. This was done at the beginning for convenience, but it is now felt that it may be the best procedure in most cases. It is recognized, of course, that a cord at constant deflection will relax in stress. In order to operate the test so that the average tension is kept constant during the tension part of the cycle, the swiveled disc can be made friction-free and held in position by a spring scale. The spring scale will indicate the tension relaxation, and the tension in the spring scale can then be adjusted to bring the tension in the cords back to the original tension.

It should be possible to produce any ratio of compression to tension. At present, the samples are mounted in a neutral position in order to make the compression and extension deflections equal. However, the samples could be mounted on the discs in a non-neutral position so that a relatively higher compression or extension would be produced.

In general, the test is run to give a 5% compression and a 5% extention. In a given test 6 samples of one kind of tire cord are tested against 6 of another kind. Figure 4 shows a typical test set up.

Failures are observed by removing the sample after any desired interval and stretching it by hand to see whether or not the cord is broken. A rubbery stretch readily reveals a broken cord. In general, the test is run for 6-hr. periods before the samples are examined for breaks. The data are given in Tables I–IV as the number of accumulated breaks with time.

Many of the tests compare different adhesive treatments on a cord from a given lot, using a dipping procedure which makes the stretch characteristics the same. For these cases there need be no concern about different initial stretch characteristics or stress relaxation differences having an effect on the relative performance of two different sets of samples which are tested simultaneously. However, in comparing two different lots of cord which have different initial stretch characteristics or stress relaxation differences, these must be recognized in any interpretation of data. An example is given in the last section of this paper.

Thus far the test has been run mostly at room temperature. For elevated-temperature testing, an oven is mounted around the discs. For the purposes of this paper the room-temperature condition is a sufficient one.

III. Factors in Tire-Cord Fatigue

The factors in tire-cord fatigue which are discussed in the final section of this paper are all connected with the adhesive treatment of rayon tire cord. Other important factors should also be mentioned.

The twist of the cord may be regarded as the first fundamental factor involved in compression fatigue. As has been indicated earlier, if no twist were present the lateral restraint of the rubber and other cord neighbors would cause the cord to behave like a rod or column. The fibers would be forced to buckle at low compression stresses. However, when the cord has twist or a spiral nature, it can behave like a spring. Longitudinal stresses, instead of leading to early buckling, will be relieved in part by the springlike folding action of the spiral plies.

An obvious factor in fatigue is the inherent quality of the material. It is inherently flexible or it is brittle; it contains either strong or weak internal forces. Interfilament friction may be another factor, and in the case of rayon this may be affected by the surface lubricant which is applied to the yarn by the manufacturer.

There are a number of factors which are connected with the problem of adhering the cord to the rubber. The tire cord reinforces the rubber tire and it is, in turn, protected from fatigue by the rubber. The individual spiral plies of the cord in a tire are coupled together with rubber and are cushioned against each other by this rubber. Cushioning should be greater when the rubber penetrates deeply between the cord plies. In the

course of compression flexing action, the rubber may be stripped from the cord; when this happens, the spiral plies are no longer protected from each other and they may abrade each other.

Before the cord is encased in rubber it is given an adhesive treatment. The adhesive used is always a combination of a hard or hard-forming material and a rubber. The hard material is generally either casein or resorcinol-formaldehyde resin, and the rubber is some form of latex or reclaimed rubber dispersion. This adhesive must be locked into the cord. The cord thus becomes modified by this penetrated material and by any excess shell of adhesive on the outside. The hard component of the adhesive stiffens any of the individual filaments that it coats and stiffens the cord as a whole. As a result, the filaments and the whole cord are more susceptible to buckling. The adhesive may also inadvertently provide hard chunks or wedges over which the filaments may be cracked during flexing action [8]. The make-up of the adhesive and the method of application are therefore very important. There is undoubtedly a connection between the stiffness factor and the interply abrasion, which was postulated earlier in this discussion as one of the contributing causes of fatigue failure. The harder the elements that are abrading each other, the more readily concentrated are the abrasion stresses. Consequently, the harder (or stiffer) the ply elements of the cord which is being subjected to a longitudinal compression, the more severe the abrasion. A stiffer cord should therefore suffer more readily from internal abrasion, as well as from buckling.

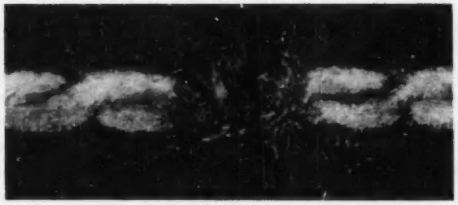

FIG. 5. *Fatigue failure of tire cord, showing region of break.*

FIG. 6. *Incipient failure of tire cord, showing separation of the cord from the rubber.*

IV. Description of Fatigue Failures

The fatigue failures obtained on the compression-fatigue machine already described are quite sharp. The failure nearly always occurs in the exact center of the sample, and the region of apparent damage is only about $\frac{1}{16}$ in. long. (See Figure 5.)

All incipient failures are evidenced by the separation of the cord from the rubber along the spiral line between the cord plies. (See Figure 6.) This spiral line between the plies is the region in which there is the greatest tendency of the cord to separate from the rubber as a result of longitudinal compression. It is also the region in which there is the severest abrasion of one cord ply against another; failure of a number of the filaments in this region also produces rubber separation. It is probable that both separation and abrasion processes go on at the same time.

V. Test Results

The principal general finding was that cord stiffness can be a factor in reducing compression-fatigue life. (See Tables I–IV.) The type of stiffness referred to is that which is imparted to the cord by the adhesive (one component of which is a hard substance).

In this investigation 1650/2 cords from two different suppliers' rayons were used. One of these rayons is designated as *A*; it has a finish which tends to resist high adhesive pickup and penetration. The other is designated as *B*; it has a finish which tends toward greater dip pickup and penetration. These cords have practically the same breaking strength and tension-fatigue lives.

One of the first things which it was desired to demonstrate was that an adhesive treatment is necessary to enable a cord encased in rubber to have a good compression-fatigue life. Cords were prepared by stringing them on a rack and brushing a particular resorcinol-formaldehyde-latex adhesive onto them, leaving $\frac{1}{2}$-in. gaps of bare cord for those which were to be tested in the bare state. The test was run on both cords *A* and *B*; the results are given in Table I.

TABLE I. FATIGUE RESULTS FOR ADHESIVE-TREATED (BRUSHED) AND UNTREATED (BARE) RAYON TIRE CORDS (5% COMPRESSION, 5% EXTENSION)

Sample	Total number of breaks after: 2 hrs.	3 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.	12 hrs.	18 hrs.
A bare	2		6					
A brushed	0		0					
A bare				5				
A brushed				0				
B bare				1		2		
B brushed				2		5		
B bare					1			
B brushed					4			
B bare				0			2	4
B brushed				0			3	6
A bare			6					
A brushed			5					
A bare	2	6						
A brushed	0	2						
A bare		3	4					
A brushed		0	1					

Although cord *A* behaved in what would be regarded as the normal manner, cord *B* performed better in the bare state than in the dipped state; the conclusion must be that the particular adhesive application used stiffened cord *B* to the point where the adverse effect was greater than any benefit derived from the adhesion to the rubber. At the same time the fatigue life of cord *B* seemed to be longer than that of cord *A*; it would appear that cord *B* was of a higher inherent quality than *A*.

However, the stretch characteristics will somewhat favor cord *B* in a fatigue test with constant deflection (as shown later), and so it would not be proper to attach too much significance to the relative results on *A* and *B*. The same should be said for the results of a direct test of bare cord *A* against bare cord *B*, in which *B* runs better than *A*. These results are not tabulated.

The cords were directly compared in another fatigue test, which had some characteristics of a compression-fatigue test. This was a particular pulley type, dead load, flex test [2, 7], called a "cord rotor test." The following are the results of testing the cords in the undipped state: cord *A*, 2.5 hrs.; cord *B*, 3.8 hrs. Based on these results and previous indications, it is postulated that rayon *B* has a higher inherent quality than rayon *A*.

From the result that bare cord *B* ran better than adhesive-treated cord *B*, it followed that the adhesive treatment should be modified so that it would produce the normal result of extending rather than of decreasing fatigue life. The more normal result was obtained by changing the method of applying the adhesive, and, to a further extent, by reducing the resorcinol-formaldehyde resin content of the adhesive by 30%. The change in method of application involved using the more normal procedure of dipping the cord in a relaxed condition and stretching it back to its original length. The data in Table II show the relaxed dipping procedure to be superior to the brushing procedure. The explanation seems to lie in the fact that in dipping the cord in a relaxed condition, followed by stretching back to the initial length, the filaments are able to swell and squeeze the adhesive to the outside of the cord plies and thereby effect a more uniform distribution on the outside region of the plies; whereas, in brushing the adhesive onto cords held in a rack, the filaments cannot swell as readily and the adhesive can actually penetrate deeper and will not be as evenly distributed on the outside of the cord plies.

By using the better adhesive treating procedure, relaxed dipping, the fatigue life of cord *B* is in-

TABLE II. FATIGUE RESULTS FOR ADHESIVE-TREATED (DIPPED) AND UNTREATED (BARE) RAYON TIRE CORDS

Sample	Total number of breaks after: 5% Compression, 5% Extension 5 hrs.	6 hrs.	12 hrs.	18 hrs.
B brushed		2	5	
B dipped		0	3	
B brushed		4	6	
B dipped		1	3	
	8% Compression, 8% Extension			
B brushed	6			
B dipped	4			
	5% Compression, 5% Extension			
B bare		3	3	6
B dipped		1	3	5
B bare		1	4	6
B dipped		0	3	4
B bare		4	5	
B lower-resin-ratio dip		0	1	
B bare		3	5	
B lower-resin-ratio dip		1	2	

creased over that of the bare cord, as indicated in Table II. By using the 30% reduced resin adhesive, the improvement becomes much more marked.

The relaxed dipping procedure and the lower-resin-content adhesive were then used for directly comparing cords *A* and *B*, and it was found in 4

TABLE III. FATIGUE RESULTS FOR RAYONS TREATED WITH LOWER-RESIN-CONTENT ADHESIVE APPLIED BY THE DIPPING PROCEDURE

Sample	Total number of breaks after: 5% Compression, 5% Extension 6 hrs.	12 hrs.	18 hrs.
A lower-resin-ratio dip	0	0	6
B lower-resin-ratio dip	0	0	6

	18 hrs.	24 hrs.	30 hrs.	36 hrs.
A lower-resin-ratio dip	2	2	3	3
B lower-resin-ratio dip	1	2	2	4

	6.5% Compression, 6.5% Extension 9 hrs.	14 hrs.	20 hrs.
A lower-resin-ratio dip	0	2	3
B lower-resin-ratio dip	1	1	5

	8% Compression, 8% Extension 6 hrs.	12 hrs.
A lower-resin-ratio dip	2	4
B lower-resin-ratio dip	1	5

TABLE IV. FATIGUE RESULTS FOR TIRE CORDS TREATED WITH ADHESIVES OF DIFFERENT RESIN CONTENTS (8% COMPRESSION, 8% EXTENSION)

Sample	Total number of breaks after: 8% Compression, 8% Extension 5 hrs.	6 hrs.	11 hrs.
B dipped		6	
B lower-resin-ratio dip		2	
B dipped	3		6
B lower-resin-ratio dip	0		2

consecutively run tests (Table III) that cord *A* did at least as well as cord *B*. It was mentioned earlier that cord *B* has stretch characteristics which would favor it somewhat in a direct test of *B* against *A*, and this is shown in the tension relaxation curves of Figure 7. Since *B* is favored and *A* nevertheless performs as well as *B*, the fatigue results can be regarded as having significance.

It was postulated that *B* was a better rayon for withstanding compression fatigue. The explanation for its not performing better than *A* seemingly lies in the stiffness factor; *B* can pick up more adhesive than *A* and can be penetrated deeper with adhesive than *A* can. In order to perform a fair test on *B*, the adhesive concentrations should be changed so that each rayon will pick up its optimum amount.

As a final illustration of the stiffness factor, the fatigue results for the higher-resin-content adhesive were compared with those for the lower-resin-content adhesive on the same cord, *B*; the lower-resin-content adhesive was shown to be definitely superior (see Table IV).

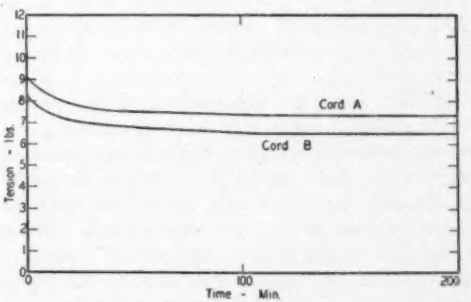

FIG. 7. *Graph of tension relaxation at 5% elongation.*

VI. Summary

A new test has been described for testing compression-tension fatigue in tire cord. Factors involved in compression fatigue have been discussed and some of them have been illustrated with test results.

Acknowledgment

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Reaction of Formaldehyde with Cotton*

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PARTIAL METHYLENATION of cotton by the reaction of cotton with formaldehyde has resulted in chemically modified cottons the new properties of which should be of practical interest. Resist threads (threads which do not dye in direct dye baths) are readily obtained by the partial methylenation of unmercerized and of mercerized cottons; in addition, an appreciable degree of resistance to biological rotting is imparted. Modified cottons with such new properties can be produced by the combination of cotton with very small amounts of formaldehyde; only slight or moderate loss of breaking strength results.

Although the possibilities of the products for specific end uses may be emphasized, the present report also brings out clearly the effects of some of the variables that are considered to be significant for "fibrous" reactions as distinguished from most reactions on chemical cellulose.

The experimental part of the work described herein is limited to one of several known general methods of bringing about the reaction of formaldehyde with cellulose. The method used brings about the reaction by heating cotton, without changing its general textile character, with formaldehyde, or a formaldehyde-yielding substance, and an acid catalyst in a nonaqueous solution with or without the presence of moisture.

One of the best reviews of the methylenation of cellulose is that by Wood [15], who also reported original work on the preparation of a completely methylenated product—cellulose monomethylene ether, with two-thirds of the hydroxyls reacted. Other reviews or discussions cover one or more pertinent aspects of the subject [3, 6, 8, 9, 12, 13, 16].

Eschalier [4] was the first to react cellulose with formaldehyde under acid conditions. While some of the reaction mixtures given in the present paper are similar to some in Eschalier's patents, his were proposed for the improvement of the strength of rayon, particularly when wet; he gave no direct suggestion that they would serve to resist cotton to dyes or impart to cotton a resistance to microbiological degradation.

Experimental Work and Properties of Products

The part of the research aimed particularly at dye-resisting was conducted at Mellon Institute. The main points brought out there were confirmed at the Southern Regional Research Laboratory; the work was continued at the Laboratory to develop products which would be resistant to microorganisms. Both series of experiments are included below.

In the initial work innumerable experiments employing a typical commercial warp mercerized yarn, natural—that is, not scoured or bleached—, were made with different solvents, different catalysts, and many changes in other variables.

Two types of reaction mixtures with acetic acid as solvent, which gave unusually good results, are illustrated by experiment Nos. 1 to 5 in Table I. Two-gram skeins of air-dry mercerized yarn were heated at the temperature of a boiling water bath in each reaction mixture, after which they were washed and neutralized with ammonia. The first two experiments were run under conditions approaching anhydrous, whereas the last three, which were run without anhydride, had appreciable amounts of moisture present. Small amounts of sodium chloride, instead of a strong acid, served as catalyst. The treated yarns remained white when subjected to dyeing with a direct fast blue 4GL, as described below; and their breaking strengths were but little affected.

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† One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I. REACTION MIXTURES AND RESULTS WITH MERCERIZED YARN

Experiment No.	Composition of reaction mixture: Acetic anhydride (ml.)	Glacial acetic acid (ml.)	Paraform-aldehyde (g.)	Sodium chloride (g.)	Time (hrs.)	Loss in breaking strength (%)
1‡	6	20	1.11	0.005*	4	none
2‡	6	20	1.11	0.005*	8	none
3	—	26	1	0.08†	4	6–7
4	—	26	1	excess, solid	4	slight
5**	—	26	1	excess, solid	4	15

* Salt added in 0.5 ml. water.
† Salt added in 0.2 ml. water.
‡ Contained small amounts of cellulose acetate.
** Contained 0.7% combined formaldehyde.

In the "final" process the best dye resists for the natural mercerized yarn, or for the same kind of yarn which had been suitably dyed, were obtained by allowing the yarn to condition at 70°F and 65% R.H. to 8½%–9% regain and then immersing the yarn in a reaction mixture, already hot, of the composition given for experiment No. 8 in Table II, in the proportion of about 100 g. of cotton to 1 l. of solution. The whole was then boiled under a reflux condenser for 1½–3 hrs., after which the yarn was drained and washed with water, followed by a dilute ammonia wash to remove both residual sulfuric acid and formaldehyde. Yarn treated in this way gave good dye-resist effects, as determined by the usual test with blue 4GL, had 90% or better retention of strength, and contained 0.25%–0.5% formaldehyde.

Exploratory tests had indicated that reaction with formaldehyde imparts to cotton an appreciably increased resistance to mildew and rotting. Research was therefore next directed toward increasing the amount of combined formaldehyde, the dye-resist effect serving merely as a simple check on the process.

The best results, experiment Nos. 11 to 13 (Table II), were obtained by simple variations of the final experiment for producing dye-resist yarns in acetone solution (No. 8). The conditioned yarn, usually in the ratio of 1 g. of yarn to 15 ml. of solution, was refluxed at the boil, usually for 4 hrs. The new conditions were not so favorable to the retention of yarn strength, but such losses as the 10%–20% observed could easily be tolerated if the treatment was found to postpone for a sufficient time a much greater loss from biological rotting. All products were resistant to dyeing.

Two mercerized yarns, a 12/4 and a 40/2, were treated according to experiment No. 13, yielding products with 1.4% and 1.3% formaldehyde contents and 25% and 19% losses of strength, respectively. These were tested for microbiological rotting by burial in soil that was active enough to completely destroy untreated cotton within 1 week. They retained 80% of their strength (treated) after 3 weeks and about 50% after 5 weeks.

It would be more practical and less expensive for commercial purposes to treat unmercerized rather than mercerized cottons, but it was found to be more difficult to retain adequate strength when treating unmercerized yarns by the final resist process (No. 8), which was so successful with mercerized yarn.

Typical results for unmercerized yarn are those for experiment Nos. 14–17 (Table III) for the treatment of 4 different yarns the reactions of which were allowed to run until moderate amounts of formaldehyde had reacted. The losses of strength, 35%–40%, were large in comparison with the usual 10% or less for the mercerized 40/2 yarn

TABLE II. REACTIONS IN ACETONE SOLUTIONS AND RESULTS WITH MERCERIZED YARN

Experiment No.	Composition of reaction mixture*: Acetone (ml.)	Formalin (ml.)	Time (hrs.)	Properties of product: Formaldehyde content (%)	Loss in breaking strength (%)
8	192	8	1.5–3	0.25–0.5	0–10
9	182	18	1	0.58	1
10	182	18	2	0.86	11
11	182	18	4	1.07	13–17
12	182	18	6	1.09	19
13	182	18 (plus excess paraform-aldehyde	4	1.2	17

* Each contained 0.2 ml. concentrated sulfuric acid.

TABLE III. REACTIONS IN ACETONE SOLUTIONS AND RESULTS WITH UNMERCERIZED YARN

Experiment No.	Unmercerized (grey) yarn	Composition of reaction mixture*				Properties of product	
		Acetone (ml.)	Formalin (ml.)	Paraform-aldehyde (g.)	Water (ml.)	Formaldehyde content (%)	Loss in breaking strength (%)
14	40/2	192	8	—	—	0.55	40
15	20/2	192	8	—	—	.49	35
16	12/3	192	8	—	—	.57	40
17	12/5	192	8	—	—	.52	38
18	12/5	198	2	—	—	.33	28
19	12/5	198	—	3.3	2	.48	25
20	12/5	198	—	9.9	2	.54	27

* Each mixture contained 0.2 ml. concentrated sulfuric acid, and each reaction ran for 2 hrs.

that had been similarly treated. The yarns resisted dyeing very well in the test with the direct blue dye.

The use of less formalin in the mixture (both less formaldehyde and less water, No. 18) resulted in less loss of strength but also less reaction between the formaldehyde and the cotton. When water and paraformaldehyde were used instead of formalin, with relatively large increases in the amount of actual formaldehyde present (Nos. 19 and 20), the amount of combined formaldehyde increased considerably but there was still a rather large loss of strength.

A few experiments were performed on unmercerized grey cotton print cloth (unbleached, containing warp size). The amount of formalin used was varied, which changed at the same time the amounts of both formaldehyde and water, and caused other obvious but less important variations. In each experiment the solution was refluxed at the boil for 1 hr. These experiments yielded dye-resist cottons with low formaldehyde contents and no loss of strength, and brought out other striking results, as typified by the data in Table IV. Among the most notable are the change in formaldehyde content through the series; the sudden loss in breaking strength between experiment Nos. 24 and 25; and the change in resist behavior from a blue tint to white at the same point.

Among the properties that have been associated with the formaldehyde-cellulose reaction are those relating to resiliency and crease-resistance, and to dimensional stability. Some improvement in these properties was shown in the methylenated cottons.

The gain of weight of cotton during the reaction is negligible for all practical purposes; when the maximum amount of formaldehyde present, about 1.5%, is all combined as the doubly linked monomer, the weight added is only 0.6%.

Moisture regain and the ability to swell of partially methylenated cotton differs with different products. When these properties were observed for a 40/2 mercerized yarn that had been treated according to experiment No. 13, which was found to contain nearly 1.5% formaldehyde and which

TABLE IV. REACTIONS IN ACETONE SOLUTIONS AND RESULTS WITH UNMERCERIZED CLOTH

Experiment No.	Composition of reaction mixture*		Strength loss		Properties of product		
	Acetone (ml.)	Formalin (ml.)	Warp (%)	Filling (%)	Resist behavior Warp	Filling	Formaldehyde content† (%)
21	192	2	10	0	Tinted	White	0.18
22	192	4	2	—	Tinted	White	.32
23	192	6	14	—	Tinted	White	.38
24	192	8	10	3	Tinted	White	.43
25	192	10	36	14	White	White	.54
26	192	12	36	—	White	White	.75
27	192	14	36	—	White	White	.69
28	192	16	36	—	White	White	.63
29	192	18	34	34	White	White	.63

* Each mixture contained 0.2 ml. concentrated sulfuric acid, and each reaction ran for 1 hr.
† Analyses of filling yarn only.

exhibited a 10–15% loss of strength, the moisture regain was about 1% less than that of untreated cotton, tested in the prevailing laboratory atmosphere; the ability to swell in water, as indicated by comparative centrifuging, was diminished by nearly half—from 43.8% retention to 23.4%.

The ability of cotton to swell in sodium hydroxide and to swell and dissolve in cuprammonium solution was found to be considerably reduced when observed on unmercerized materials that had been treated according to experiment Nos. 21, 24, and 25 (Table IV). With sodium hydroxide of mercerizing strength, the activity of the fibers upon swelling, which was observable under the microscope, was less for the first sample of the series than for the untreated cotton and decreased progressively with increase in formaldehyde content. When tested with cuprammonium solution of a strength which would dissolve the untreated cotton in a few seconds, the first in the series of treated cottons showed some resistance to swelling and dissolving, whereas the last required somewhat more than 5 min. to dissolve. These materials were sufficiently methylenated to yield complete dye resists—the tinting of the first two being due to warp size, which is discussed below.

Discussion of Experiments and Properties of Products

Materials and Procedures

There were two main reasons for using natural cotton (grey yarn or fabric) and natural mercerized yarn rather than purified cellulose: firstly, it was desired to make new products from such cottons directly; secondly, as soon as natural cotton is given any treatment, as, for example, for its purification, it may be changed in some other fundamental manner which may change its response to treatment for chemical modification, especially when its fibrous form is to be maintained.

Such changed responses, which often have been quite unexpected, are well illustrated by methylenation reactions performed comparatively (according to experiment No. 1 in Table I) on cottons that had been treated merely by commercial finishing processes. The original unmercerized (raw) cotton resisted well but was seriously tendered; kier-boiled and bleached (purified) yarn failed to yield complete resists; whereas, in contrast, mercerized natural yarn was well resisted and exhibited full retention of strength.

Furthermore, a given treatment may have different effects on yarns which are supposed to be similar. For example, when treated according to experiment No. 10, Table II, a yarn that had been mercerized in the laboratory by a method simulating that used for the commercially mercerized yarn underwent losses of strength 3 times as great, and had only about four-fifths as much combined formaldehyde. On the other hand, samples from different lots of commercial warp mercerized yarn from one plant usually gave consistent and "repeatable" results.

Ordinary commercial formalin with an undetermined amount of methanol was used, but the methanol probably had no particular effect since paraformaldehyde (with no free methanol) has been found to be interchangeable with formalin when similar amounts of water are present. Neither was any precaution taken to exclude formic acid since small amounts have been found not to act as a catalyst for the reaction of formaldehyde on cotton.

Marsh and Wood ([10], p. 134) warn against the possibility of mistaking any free polymerized formaldehyde being firmly held by cellulose for combined formaldehyde; but this possibility seems not to have entered seriously into the present case. Considering the known properties of formaldehyde [14], it is probable that free lower polymers would either not be deposited on the cotton to any extent in the presence of acetone, or would be readily removed by the usual dilute ammonia washing. Nor would small amounts of high polymers be expected to contribute appreciably to dye-resisting. As a rough check, 10 representative resisted yarns were refluxed, according to the method of Wood [15] for removal of free formaldehyde, for 30 min. in 20% ammonia. There was no decrease in resisting effect when they were included in dyeings by the usual method with samples of the same yarn which had been rinsed in dilute ammonia but not refluxed.

The removal of free formaldehyde is important in preparation for chemical analysis and would be necessary for methylenated cotton to be used in clothing or in bags for food. On the other hand, the leaving-in of any uncombined formaldehyde might be an advantage in cotton intended to be mildew- or rot-resistant, since it might help postpone attack by microorganisms.

Weakening of the cotton is caused, partly at least, by acid hydrolysis, and this is indicated by an increase in copper number; but it is no doubt also partly due to so-called "embrittlement," which, in turn, is due to changes in the elastic properties of the fibers that result in unfavorable stress distribution, as, for example, during breaking-strength tests.

Effects of Water in Reaction Systems

Partial methylenations of cotton have been performed in solutions that were initially "dry" before entry of the air-dry cotton with its ordinary content of moisture, and it seems clear from the experiments of Table I that no large amount of water is necessary for the reaction.

Actually, the reactions to produce dye-resisting by means of formalin in acetone were performed in the presence of more water than formaldehyde. Also, an increase in the amount of formalin present meant a considerable increase in the amount of water, although it resulted in a product with more combined formaldehyde. This behavior seems consistent with the view that the reaction with cellulose takes place with the monohydrate or methylene glycol form of formaldehyde [2], although the results obtained with solutions containing very little water raise the question of whether the presence of any appreciable amount of the glycol form is necessary. Regardless of the form of the formaldehyde, differences in the amounts of moisture in both yarns and reaction mixtures can influence the reaction, as readily shown by the dye test, sometimes very greatly; but moisture in the yarn is not equivalent to moisture in the reaction mixture. For example, in preparing dye-resist threads, the usual mercerized yarn with 5%–6% moisture (regain) and similar yarn with 7½%–8½% moisture came out differently, that with the lower regain being incompletely resisted and showing a blue tint in the dye test.

Since the moisture in both of these yarns entered the reaction system and supposedly approached an equilibrium, it is evident that the different amounts of water present initially affected the results. Such effects seem to be attributable to some difference in the manner in which the different amounts of water are held in the cotton, and quite possibly to a difference in the initial degree of swelling.

That the initial state of swelling of the cotton can have a decisive influence on the nature of the product was readily shown in the following experiments. One skein of mercerized yarn was prepared by a thorough wetting in water and squeezing to 45%–50% regain, and another by wetting followed by displacement of the water with several changes of acetone. The wet, swollen skein and the dewatered skein were then both put into a reaction mixture (No. 24, Table IV) at the same time with an air-dry skein, and the whole system was refluxed for 4 hrs. A similar set of yarns was treated in a mixture (No. 29) containing more formalin (more water as well as more formaldehyde). Except for the initial treatments of the yarn, the experiments were run as usual.

The results of the two experiments were almost alike. The yarns that were put air-dry into the solutions were both well-resisted but contained relatively small amounts of formaldehyde—0.5% to 0.8%. On the other hand, the preswollen yarns, those entered with and without water, were not resisted but dyed to about half the depth of shade of the original mercerized yarn and contained much more formaldehyde than the resisted yarns—about 1.4%. In both experiments the resisted yarns were the strongest (5%–15% strength losses); the yarns entered wet were the weakest (30% strength losses); and those dewatered by acetone were of intermediate strength (12%–20% losses).

These experiments emphasize two things: (1) Water in the cotton and that in the reaction mixture are not equivalent, because the water in the yarn went into the reaction mixture, and if it had merely represented a little more water, the yarns treated together in each group should have come out alike. (2) The difference between the resulting yarns that resist and those that dye depends largely upon the state of swelling of the cotton when it enters the reaction mixture. The cellulose (cotton) which is put in wet remains in an open or porous state and may be regarded as being swollen; that which is dewatered by acetone apparently remains in a similar state during the reaction. These cottons were in a sufficiently swollen state in the dye bath to take up color, while the resisted yarn was not.

Wood [15] recognized two types of product of the reaction of formaldehyde on cellulose—one which swells considerably in water and dyes darker than normal, and one which does not swell and resists dyeing. Of both cotton and rayon, Wood says ([15], p. 415T): "The amount of moisture

present when the reaction is arrested determines whether the product is of the dye-resisting or the dye-absorbing type." Apparently this is not the whole story, at least not for the reactions with cotton, because in each of the experiments just described, yarns which dyed to medium shades and yarns which entirely resisted the dye were both present in the same solution at the completion of the treatment and both were subject to the influence of the same water. Hence, the determining factor must be sought elsewhere, and this factor seems to be swelling.

Nature of Reactions and Products

There are several possible ways in which chemically combined formaldehyde may have reacted with cellulose; these are discussed by Schaeffer [12] and summarized by Gruntfest and Gagliardi [5]. Formaldehyde molecules may be added to cellulose singly or as chains at single hydroxyl groups to form methylol or hydroxypolyoxymethylene groups; they may be reacted between hydroxyl groups in a given cellulose chain to form rings; or they may be reacted between hydroxyls in different chains to form cross-links.

One of the most striking and significant points bearing on the mode of combination of formaldehyde with cotton is the relatively great effect obtainable by very small amounts of formaldehyde —for example, complete dye-resisting with 0.5% (or less) formaldehyde. If the formaldehyde reacts with cellulose to form a methylene ether (R—O—CH_2—O—R), each molecule of formaldehyde would combine through 2 hydroxyl groups in the ratio of 1 to 36 glucose units. The formaldehyde might form one ring or one cross-bond per 36 glucose units, thus blocking only 1 out of every 54 hydroxyl groups in the cellulose. If, however, as is probable, most of the reaction takes place in and around the amorphous cellulose, the cross-bonding in the cotton would be concentrated in these critical regions.

That the union between formaldehyde and cellulose in the dye-resisting cotton consists to a significant extent in cross-bonding follows from the observed relationships between partially methylenated cotton and direct dyes. Direct dyeing of cellulose is commonly regarded as being associated with its hydroxyl groups, and dye-resisting with a reduction in their number. If the resisting by formaldehyde-treated cotton were a simple matter of blocked hydroxyls it would seem immaterial whether the methylene ether group were present in a ring or as a bond between chains because the same number of hydroxyl groups would be affected in both cases.

But a comparison with the direct dye-resisting behavior of partially acetylated cotton will indicate that more than a mere blocking of hydroxyl groups is involved in the formaldehyde resists. With partial acetates there is no sharply defined point where dye-resisting is complete, but good results are obtainable for cottons with between 15% and 18% acetyl content, where 1 hydroxyl out of 4 or 5 is blocked. It is evident that far more hydroxyls must be reacted with acetyl groups than with formaldehyde in order to produce a resist. Since both reactions probably take place mainly in the amorphous regions of cellulose, which are also regarded as the seat of the dyeing, some factor other than the direct blocking of hydroxyls must contribute to the dye-resisting that is accomplished by formaldehyde treatment, by rendering the relatively large number of remaining free hydroxyl groups inert to dyeing.

Moreover, if the formaldehyde were combined as hydroxymethyl ether groups, or as side chains of polymerized formaldehyde ending in hydroxyl groups, no pronounced loss in dyeing capacity would be expected, because there would be no net loss of hydroxyls. Also, if the formaldehyde were present in doubly linked form in closed rings, each formaldehyde molecule blocking a pair of hydroxyls in a cellulose chain, there would be far too few of them for resisting, in view of the much greater number of blocked hydroxyl groups which are necessary in partially acetylated cotton.

It seems most probable, therefore, that the great effect of relatively small amounts of combined formaldehyde on direct dyeing is due mainly to cross-linking, which interferes with the swelling of the cotton in the water of the dye bath in such a way as to prevent access of the dye molecules to the interior of the cotton fiber cellulose, as implied in earlier literature and suggested more definitely in recent publications [3, 5]. Hence, dye-resisting by small amounts of combined formaldehyde supports the idea of a cross-linking mechanism.

Further evidence of cross-linking in partially methylenated cotton is afforded by colored dye-resist threads. These are made by dyeing cotton

yarn with direct dyes (not fast to hot water) and methylenating the dyed material; after this treatment the yarn not only does not take on new color when subjected to another dye bath but also does not lose its own color, which originally had been fugitive. This fastening of direct dyes seems to be best explained by the theory that the dye molecules are held in a pore system in cellulose which cannot swell to a sufficient degree to allow their diffusion outward because of cross-bonding. Alternative possibilities, such as direct improvements in fastness being caused by the reaction of formaldehyde on the dyes or by bonding between dye molecules and cellulose, seem inadequate to account for the pronounced improvements in fastness observed, although they have not yet been proved to be inoperative.

Hence, the formation of cross-links between chains during the formaldehyde treatment of cellulose, first suggested by Meunier and Guyot [11] and generally accepted today, is indicated by direct dye-resisting and dye fastening, as well as by tests on swelling.

Retention of Strength of Cotton

The experiments on unmercerized print cloth, described on p. 57, brought out clearly the possibility of partially methylenating natural cotton without loss of strength, within a fairly definite range of conditions.

The filling of the cloth from the first treatment in the series (No. 21) exhibited complete resisting, obtained with a very small amount of formaldehyde in the reaction mixture (hardly 0.4% by volume); only a small amount of formaldehyde was combined with the cotton and there was no appreciable loss of strength. In the series, however, there was the sudden drop in the strength of the cloth between experiment Nos. 24 and 25, where there was also the change from a blue tint to white upon dyeing; close inspection, however, showed that it was the warp threads which were dyed blue, and that the filling threads were white even in the cotton that had been treated with the smallest amount of formaldehyde.

It seems to follow that the drop in strength with greater amounts of formaldehyde was due to more active hydrolysis after some particular concentration of water was reached in the acetone solutions. The blue dye in the tinted dyeings (Nos. 21–24) was obviously associated with the warp size (starch). It failed to appear at about the same point where pronounced tendering of the cotton began, which, together with qualitative tests for starch, indicates that the starch had become hydrolyzed by that time and had come off the cloth, or at least had failed to dye. Hence, under the particular conditions of these experiments, the starch and dye apparently acted as an indicator of hydrolysis and tendering of the cotton.

Methods of Testing Formaldehyde-Treated Cottons

The simplest and most convenient breaking-strength tests on yarn or cloth under the usual conditions of 65% R.H. and 70°F served to detect any severe tendering and also to provide the relative values for treated and untreated materials.

The analysis for formaldehyde was performed according to the method of Hoffpauir, Buckaloo, and Guthrie [7], by the hydrolysis of the partially methylenated cotton with concentrated sulfuric acid and the colorimetric estimation of the formaldehyde in the hydrolyzate, using Schiff's reagent. Each sample, the formaldehyde contents of which are included in Tables I–IV, had been through a direct-dye bath without taking up color prior to its analysis, which furnishes the added assurance of the absence of free formaldehyde. The analytical results given are for air-dry cotton; these would be 5%–8% higher if they were adjusted to the dry basis.

For ordinary routine dye tests, such as for following the course of the reaction or for checking the uniformity of treatment, a simple direct dyeing can be made with any color found to be sufficiently resisted by partially methylenated cotton. The tests are usually made with a direct fast blue 4GL ([1], Prototype 26). For convenience, samples of the treated yarn or cloth and of an untreated control are stapled or sewn to an ordinary piece of cotton cloth which is large enough so that variation in the dyeing capacity of the unknown samples will not cause great differences between the final bath conditions from one dyeing to another.

The bath is 30 times the weight of the cotton, and the dyeing is made with 2% dyestuff and 20% C. P. sodium chloride, calculated on the weight of the cotton, for 30 min. at the boil.

Summary

Partially methylenated cottons have been prepared by the reaction of cotton with formaldehyde under acid conditions in nonaqueous (mainly acetone) solutions. Although it does not differ from ordinary cotton in appearance and general textile character, the modified cotton displays new properties even at relatively low formaldehyde contents—from 0.5% to 1.5%—which may prove to be of practical importance.

The progress and uniformity of the reaction can be followed not only by analysis for combined formaldehyde, but also very conveniently by a determination of the reduction in the capacity of the cotton for taking up a direct dye. This work affords an excellent example of the possibilities of such dyeing techniques.

Dye-resisting yarns of possible technological interest can be produced. The dye-resisting effect appears to be mainly due to cross-bonding in the cellulose.

The treated cotton has a decreased swelling capacity in water and in other agents which swell or dissolve cotton.

Products of sufficient formaldehyde contents have good resistance to biological rotting.

Direct cotton dyes are made faster by the treatment.

The cotton tends to lose strength as a result of acid hydrolysis and "embrittlement," but adequate strength can be retained for its prospective uses.

Effects of moisture that is originally present in the cotton and in the reaction mixtures indicate that the state of swelling of the cotton at the time of treatment is especially significant in determining the properties of the reaction products.

Methods described can be employed for the production of partially methylenated cottons of good uniformity and low degrees of substitution.

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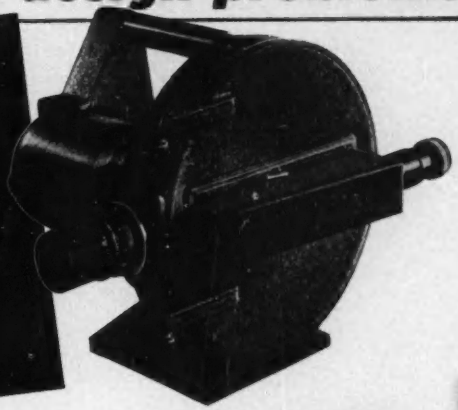

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